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**Evaluation of Combustion Variable
Effects on NOx Emissions from Mineral Kilns**

KVD, Inc., Irvine, CA

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EVALUATION OF COMBUSTION VARIABLE EFFECTS
ON NO_x EMISSIONS FROM MINERAL KILNS

by

R. J. Tidona, W. A. Carter, H. J. Buening,
S. S. Cherry, M. N. Mansour

KVB, Inc.
18006 Skypark Boulevard
Irvine, California 92714

Contract No. 68-02-2645

EPA Project Officer: Robert E. Hall

Industrial Environmental Research Laboratory
Office of Environmental Engineering and Technology
Research Triangle Park, NC 27711

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ABSTRACT

Results of tests performed on a lime kiln, precalciner cement kiln and conventional wet process cement kiln are presented and discussed. Where applicable, the effectiveness of excess air variations on pollutant emissions are quantified and compared to previous results. Mass balances were also calculated for the two cement kilns.

Lower excess air (oxygen reduced from 4.4 percent to 2.8 percent) was found to produce a 23 percent reduction in NO_x for the lime kiln. A linear regression of the data obtained for a conventional coal-fired wet process cement kiln predicted a 38 percent NO_x reduction when the oxygen was reduced from 2 percent to 1.5 percent. However, a regression of the data predicted a 47 percent increase in SO_2 emissions when the O_2 was lowered over the same range. Combustion modifications were not implemented on the precalciner cement kiln.

A combustion tunnel was designed, fabricated and operated to determine the effect of burner operating variables on cement kiln near-flame NO_x production. The effects of combustion air preheat, carrier air dilution and fuel injection velocity were the primary variables assessed for both natural gas and coal.

At the subscale level, reducing the carrier air oxygen content from 20.9 percent to 11 percent had a significant effect on NO_x , reducing the emissions by 19 percent. Lowering the fuel injection velocity from 61.0 m/s (200 ft/sec) to 30.5 m/s (100 ft/sec) reduced NO_x by 37 percent. Reducing the combustion air temperature also has a significant impact on NO_x emissions. However, this may not be a viable control on economic grounds.

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Limitations on Application of Data Reported

The pollutant emission data cited in this report pertain to specific classifications of mineral kilns. These data should not be used to estimate mean emissions from other kilns or to predict emission reduction potentials of combustion modifications until the modifications have actually been carried out on several other kilns. The NO_x reductions have been demonstrated during short duration tests. Long-term effectiveness, including potential adverse impacts on product quality, must be assessed.

SECTION 1.0

INTRODUCTION AND SUMMARY

This final report is one of a series which describe tests of combustion modifications to control NO_x emissions from industrial process equipment. This work was performed under EPA Contract No. 68-02-2645 over the time period from August 1977 to June 1981.

The activities reported herein include tests performed on a rotary lime kiln (Location 6), precalciner cement kiln (Location 8), and conventional wet process cement kiln (Location 9). Fuel oil was used in the lime kiln while both cement kilns used coal.

Variation in excess air was the NO_x control implemented on the lime kiln and wet cement kiln. Only as-found* tests were performed on the precalciner kiln since this kiln had just recently been started up and its operation may not have been fully optimized.

For the lime kiln (Location 6), a reduction in excess air (oxygen lowered from 4.4 percent to 2.8 percent) reduced NO_x emissions by 23 percent. Further reductions in excess air produced a lime clinker of poor quality. A new oil tip (with fewer orifices to delay fuel/air mixing) resulted in oil impinging on the kiln wall -- an unacceptable operating condition.

As-found testing on the precalciner cement kiln (Location 8) resulted in NO_x levels higher than the conventional wet process kiln tested at Location 9. This result may be due to kiln operation not being fully

*As-found conditions are those found by the KVB field test crew at the time of their arrival at the site. Baseline conditions are those corresponding to nominal unit operation. In most instances as-found and baseline operating conditions are the same, however, they can differ. Changes in unit operation to achieve baseline conditions are not interpreted as a combustion modification.

optimized at the time of the test program. Mass balances were performed for sulfur, sodium and potassium by a contractor retained by the plant operator. Closure on these balances was good.

Testing at the conventional wet process cement kiln (Location 9) included as-found conditions, baseline conditions and variations in oxygen level. Linear regression analysis of the NO_x data would predict a 38 percent reduction in NO_x when the oxygen level was lowered from 2.9 percent to 1.5 percent. However, a simultaneous increase in gaseous SO_2 of 47 percent was also predicted. Mass balances were made on seven kiln constituents with the largest single difference being 29.5 percent. The composite weighted difference for all seven constituents was 3.8 percent.

A combustion tunnel was constructed and tested to determine the effect of burner parameters on cement kiln near-flame NO_x levels for both natural gas and coal fuels. It was determined that combustion air preheat, fuel injection velocity, and oxygen content of the primary combustion air stream have first-order effects on NO_x levels. The subscale program results will be used to select advanced combustion modifications for implementation at the pilot scale.

1.1 COMPARISON OF PREVIOUS AND PRESENT CEMENT KILN PROGRAMS

KVB, during the previous EPA contract (Reference 1) and a contract for the California Air Resources Board (Reference 2) performed emission measurements on two conventional kilns. Table 1-1 summarizes the results obtained on all four kilns tested.

Of note for Location 3 is the higher NO emissions with natural gas fuel as opposed to either oil or a combination of coke and natural gas. A similar situation has been measured in glass furnaces (Reference 3) where NO emissions from natural gas firing are higher than from oil firing despite the fuel-bound nitrogen content of oil fuel. One possible explanation for this difference would be due to the higher radiant flame cooling for an oil or coal flame because of higher emissivity. The more rapid flame cooling would suppress the NO production.

TABLE 1-1. COMPARISON OF CEMENT KILN NO EMISSIONS

Location	Process	Fuel	Condition	NO			Reference
				ppm, dry @ 3% O ₂	kg/Mg Clinker	(lb/ton)	
3	Dry	Coke + Nat. Gas	Baseline	1014	4.0	(8.0)	1
3	Dry	Nat. Gas	Baseline	1460	7.5	(14.9)	2
3	Dry	Oil	Baseline	640	3.3	(6.6)	2
9 (2144)*	Wet	Nat. Gas	Baseline	2474	9.1	(18.2)	1
8	Precalciner	Coal	As-found	1264	3.7	(7.5)	This report
9 (2645)*	Wet	Coal	Baseline	183	0.88	(1.8)	This report

*9 (2144) = Location 9, Contract 68-02-2144

9 (2645) = Location 9, Contract 68-02-2645

Of equal note is the very low NO value measured during the present EPA contract for the coal-fired wet process kiln. A review of the testing procedures indicated that all measurements were properly made. At present there is no explanation why this particular kiln is such a low NO emission source.

SECTION 2.0

TEST EQUIPMENT DESCRIPTION

2.1 EMISSIONS SAMPLING EQUIPMENT

Gaseous emission measurements for the full-scale tests were made using analytical instruments and equipment contained in a government-furnished mobile instrumentation laboratory. A plan view of the trailer is shown in Appendix A. Total particulate measurements were made using an EPA Method 5 sampling train manufactured by Andersen Samplers, Inc. Particulate size distribution was measured using an Andersen Mark III Cascade Impactor. Total oxides of sulfur were measured by wet chemistry methods using the sampling train and analytical procedure of the Goksoyr-Ross method. Smoke density was measured using an automated Bacharach smoke spot pump. Stack opacity readings were made during particulate tests according to EPA Method 9. The subscale cement kiln measurements were made with instrumentation permanently installed in KVB's laboratory, and are described in Section 6.0.

2.1.1 Gaseous Emissions Sampling System

The mobile laboratory is equipped with analytical instruments to continuously measure concentrations of NO, NO₂, CO, CO₂, O₂, SO₂, and hydrocarbons. The sample gas is delivered to the analyzers at the proper condition and flow rate through the sampling and conditioning system described below. Appendix A describes the analytical instrumentation and the details of the sampling system.

A flow schematic and description of the flue gas sampling and analyzing system is presented in detail in Appendix A. Briefly, the sampling system used pumps to continuously draw flue gas from the heater into the laboratory. A high-capacity heated positive displacement diaphragm pump was used to draw a high volume of flue gas into the analyzers thereby providing adequate system response.

Special precautions were required to obtain a representative sample for the analysis of NO₂, SO₂, and hydrocarbons. These precautions consisted

primarily of insuring that the sample was kept above its dew point, since these constituents are quite soluble in water. For this reason, an electrically heated 9.5 mm (3/8 in.) Teflon sample line was used to bring the sample into the laboratory for analysis. The hot pump provided heated sample directly to the hydrocarbon, SO₂, and NO_x analyzers.

A portion of the sample pump discharge was also sent through a refrigerated condenser [to reduce the dew point to 275 K (35°F)], through a large rotameter with flow control valve, and then to the O₂, NO, CO, and CO₂ instrumentation. Flow to each individual analyzer was measured and controlled with smaller rotameters and flow control valves. Excess sample was vented outside the laboratory.

2.1.2 Particulate Emissions

Particulate samples were taken at the same sample location as the gas sample using an Andersen Samplers, Inc. portable effluent sampler. These tests were made at baseline and optimum low-NO_x operating conditions. This system, which meets EPA design specifications for Test Method 5, Determination of Particulate Emissions from Stationary Sources (Federal Register, Volume 36, No. 27, page 24888, December 23, 1971) was used to perform both the initial velocity traverse and the particulate sample collection. Dry particulates were collected in a heated case that contained a 110 mm glass-fiber filter for retention of particles down to 0.3 micrometers. Condensible particulates are collected in a train of four impingers in a chilled water bath.

Particle size was measured at baseline and optimum low-NO_x conditions at the same sample location as the Method 5 tests. An Andersen Mark III Cascade Impactor was used for all of the sizing tests because of its high-volume/low grain loading capability. This impactor was capable of fractionating particles in situ into nine aerodynamic size ranges (eight collection stages and one backup filter). The size range capability of this impactor was approximately 0.4 µm to 10 µm.

The Method 5 sampling train and procedures, and the impactor operational procedures, are discussed in Appendix A.

2.1.3 Wet Chemical SO_x Measurement

The Goksoyr-Ross technique was used to sample the stack gas for SO₃. This method uses controlled condensation of the stack gases in a coil maintained at 333-344 K (140-160°F) by a water bath. This temperature is below the sulfuric acid (H₂SO₄) dewpoint so that the SO₃ and the water vapor in the flue gas condense upon the coil walls to form H₂SO₄ droplets. The SO₂ in the flue gas passes through the coil and is collected in impingers containing a weak hydrogen peroxide solution. Following the impingers, the flue gas flows through a dry gas meter and is then discharged into the atmosphere.

The coil rinse and impinger liquid are each analyzed by means of an acid-base titration with a sodium hydroxide solution. Thus, both the SO₃ and SO₂ concentrations may be determined from this procedure. By comparison EPA Method 6 yields values for SO₂ only.

2.1.4 Smoke Spot and Opacity Measurement

On combustion equipment where smoke numbers normally are taken, such as oil-fired boilers, KVB, Inc. determines the smoke number using test procedures according to ASTM Designation: D 2156-65. The smoke number is determined at each combustion modification setting of the unit. Examples are baseline, minimum excess air, low load, etc., and whenever a particulate concentration is measured.

Smoke spots are obtained by pulling a fixed volume of flue gas through a fixed area of a standard filter paper. The color (or shade) of the spots that are produced is visually matched with a standard scale. The result is a "Smoke Number" which is used to characterize the density of smoke in the flue gas.

Opacity readings are taken by a field crew member who is a certified graduate of a U.S. Environmental Protection Agency approved "Smoke School." Observations are made at the same time that particulate measurements are made and as often in addition as deemed necessary to gather the maximum amount of information. The procedures set forth in EPA Method 9, "Visual Determinations of the Opacity of Emissions for Stationary Sources," are followed.

SECTION 3.0

ROTARY LIME KILN - LOCATION 6

This kiln is part of a pulp and paper facility and functions to produce the lime (CaO) which, after slaking, reacts with soda ash (Na_2CO_3) to form the caustic soda (NaOH) used in the wood digester.

The feed to the lime kiln consists of the CaCO_3 byproduct from the NaOH reaction ("lime mud") and additional limestone (CaCO_3). The feed moisture content is approximately 35 percent by weight, and on a dry basis limestone is 90 percent of the feed.

The lime kiln in many respects resembles a conventional wet process cement kiln, both as to form and function. A single burner at the clinker (product) end of the kiln fires countercurrent to the feed motion, with the burner having both primary and secondary air circuits. There was no capability to measure either air flow. The wet feed undergoes drying and calcination (conversion of limestone to lime) but not the clinkering chemical reactions performed by a cement kiln. The other major difference was that the lime kiln used ambient temperature combustion air for both primary and secondary circuits as the kiln did not have a product cooler. The lime kiln was equipped with two "odor gas" ports at the burner end to dispose of hydrogen sulfide (H_2S) rich waste gas. This stream, which was intermittent in usage, represented a negligible fraction of the total heat input.

The kiln is 3.5 m (11.5 ft) in diameter, 83.8 m (275 ft) long and is equipped with a single steam atomized burner firing #6 oil. (Table 3-1 is the fuel oil ultimate analysis.) A wet scrubber is used for particulate control and all emission measurements were performed upstream of the scrubber.

Table 3-2 summarizes all the test data while Figure 3-1 illustrates the effectiveness of lower excess air on NO emissions. The column headed "Kiln Front End Temp." are optical pyrometer measurements made of the kiln interior temperature at the burner end of the kiln. The data shown in

TABLE 3-1. LOCATION 6 FUEL OIL ULTIMATE ANALYSIS

	<u>% By Weight</u>
Carbon	89.69
Hydrogen	7.65
Nitrogen	0.39
Sulfur	1.71
Ash	0.030
Oxygen (by difference)	0.53
Gross Btu/lb (kJ/kg)	17,220 (40,050)
Net Btu/lb (kJ/kg)	16,520 (38,430)

TABLE 3-2. SUMMARY OF GASEOUS EMISSIONS FROM A LIME KILN - LOCATION 6

Test No.	Date 1979	Process Type	Fuel Flow m ³ /h	O ₂ %	CO ₂ %	NO _x ppm Dry at 3% O ₂	CO ppm Dry at 3% O ₂	SO ₂ ppm Met	Kiln Front End Temp. K	Comments
6/1-1	10-25	49.1	1.63	4.4	19.9	90	33	-	1,402	Baseline
6/1-2	10-25	49.1	1.44	2.8	20.5	69	25	-	1,478	Minimum Primary Air
6/1-3	10-25	48.6	1.48	1.5	20.5	13	17	-	1,478	Low O ₂
6/1-4	10-25	49.1	1.21	6.5	18.3	160	20	-	1,478	High O ₂
6/2-1	10-25	49.1	1.21	4.7	18.8	119	20	-	1,478	Baseline
6/2-2	10-25	49.1	0.57	11.0	9.8	192	18	-	1,267	Low Fire
6/2-3	10-25	49.1	1.82	3.4	20.0	132	15	-	1,200	High Fire
6/3-1	10-25	49.1	1.21	4.0	19.2	113	13	-	1,436	Baseline
6/3-2	10-25	49.1	1.17	3.9	18.6	92	28	-	1,339	Increased Secondary Air Flow
6/3-3	10-25	49.1	1.21	3.2	20.5	77	33	-	1,353	Low O ₂
6/3-4	10-25	49.1	1.19	3.8	18.9	104	33	-	1,367	Baseline Repeat
6/4-1	10-26	48.6	1.21	4.5	20.5	158	49	-	1,422	Baseline without secondary air
6/4-2	10-26	48.6	1.17	6.0	18.0	246	54	-	1,300	High O ₂ without secondary air
6/4-3	10-26	48.6	1.21	3.0	21.0	90	45	-	1,381	Medium O ₂ without secondary air
6/4-4	10-26	48.6	1.21	1.3	22.0	60	2,165	-	1,464	Low O ₂ without secondary air
6/4-5	10-26	48.6	1.21	5.0	20.5	105	81	-	1,436	Baseline with minimum secondary air
6/4-6	10-26	49.1	1.17	5.8	18.8	115	62	-	1,378	High secondary air
6/4-1A	10-26	49.1	1.21	4.2	19.6	154	54	-	1,356	Baseline without secondary air
6/4-7	10-26	49.1	1.21	1.6	20.5	108	71	-	1,467	No secondary air - no odor gas
6/5-1	11-12	34.1	1.32	5.8	20.5	127	41	50	1,378	Baseline old oil tip
6/6-1	11-12	34.1	1.32	5.4	20.5	156	33	40	1,467	Baseline new oil tip
6/6-2	11-12	34.1	1.14	3.5	20.5	110	22	43	>1,478	No secondary air - new oil tip
6/6-3	11-12	34.1	1.14	4.2	20.5	119	18	38	1,450	No secondary air - no odor gas
6/6-4	11-12	34.1	1.14	4.8	20.5	138	15	110	1,461	No secondary air, High O ₂ - no odor gas
6/6-5	11-12	34.1	0.40	6.7	16.0	162	16	105	1,456	Minimum secondary air - with odor gas
6/6-6	11-12	34.1	1.14	6.1	19.2	147	20	95	1,417	Min. sec. air low pres. air with odor
6/6-7	11-12	34.1	1.14	4.2	20.2	124	12	44	1,444	Minimum secondary air - no odor gas

gal/min = m³/h • 4.40

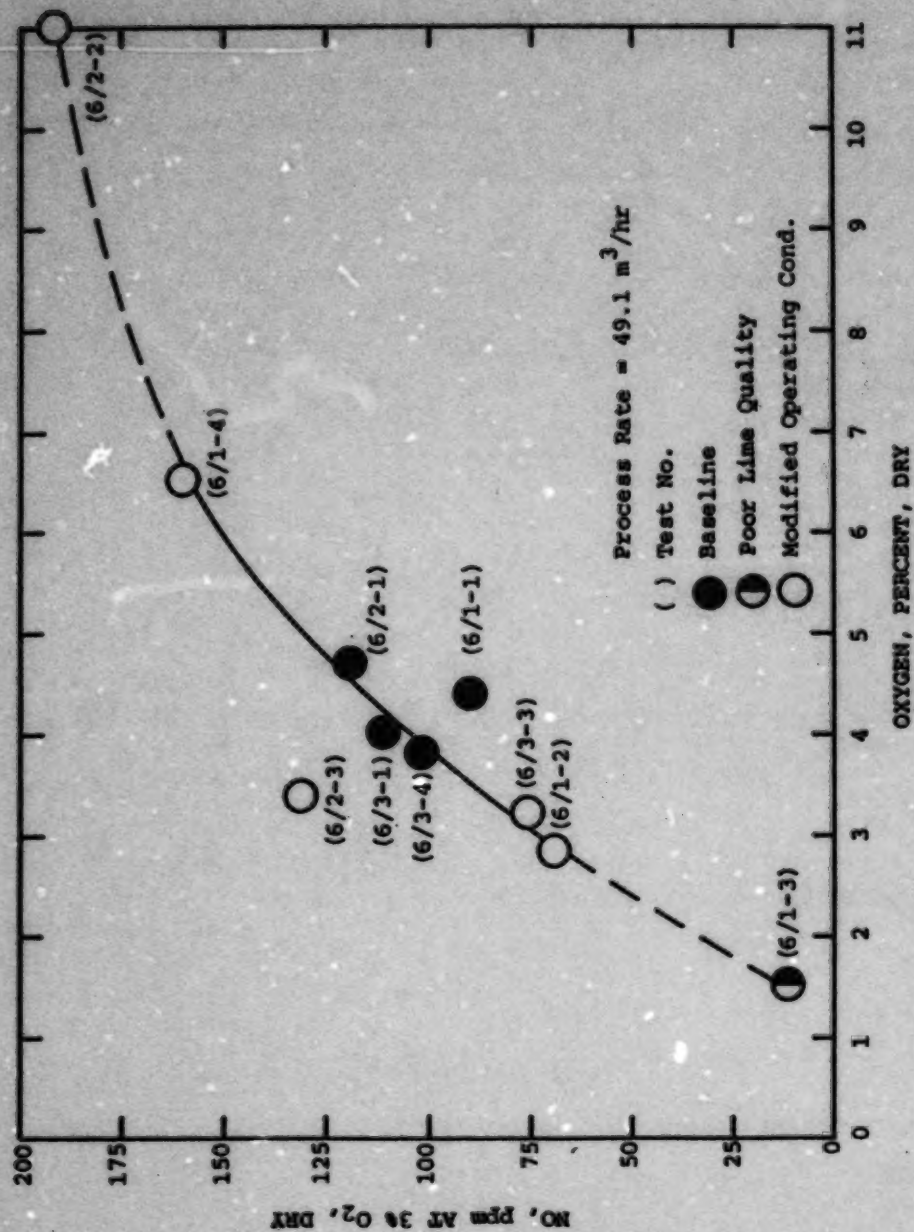


Figure 3-1. Location 6 Lime Kiln - Effect of O₂ on NO

Figure 3-1 correspond to a constant process rate of $49.1 \text{ m}^3/\text{h}$. Also of note is the variation in the baseline results, with such variation not being unusual for industrial combustion equipment. This baseline variation requires that the combustion modification test results be referenced to the baseline obtained nearest in time. As noted, a reduction in oxygen from 4.4 percent to 2.8 percent (test 6/1-2 vs. test 6/1-1) produced a 23 percent decrease in NO emissions ($13.1 \text{ ppm NO}/\% \text{ O}_2$), while a 86 percent decrease in NO was measured when the oxygen was reduced to 1.5 percent (test 6/1-3). However, at the latter conditions the lime quality was poor.

Tests 6/2-2 and 6/2-3 are of uncertain accuracy as they were performed during a ± 50 percent change in fuel flow rate. The possibility exists that insufficient time was allowed after the fuel flow rate change to permit the kiln to stabilize thermally. The lower kiln front end temperature for test 6/2-2 with respect to 6/2-1 is most likely a consequence of the reduced fuel flow rate. However, the still lower temperature for test 6/2-3 probably reflects an unstabilized kiln operating condition.

If this was indeed the situation, then it is presumed that the NO measured for test 6/2-2 was too high and that for test 6/2-3 was too low. This is a consequence of the kiln internal temperatures not being representative of the fuel flow rate.

The total kiln air flow is in two parts: a primary supply coaxial with the oil gun and; a secondary circuit distributed around the kiln interior. Each circuit is supplied by its own fan. Test 6/3-2 was conducted by increasing the secondary flow and decreasing the primary flow while maintaining the overall O_2 at 3.9 percent. Reducing the primary air flow (which is in immediate proximity to the fuel flow) has the effect of delaying the combustion process and suppressing the peak flame temperature. This, in turn, reduces the NO production. With respect to the nearest baseline (test 6/3-1) this reduced the NO emissions by 19 percent. Reducing the total air flow by closing down on both the primary and secondary air dampers (test 6/3-3) reduced the NO emissions by 32 percent. This modification is consistent with just lowering the excess air level for which the NO sensitivity was 21.4 ppm

NO/% O₂. However, lime quality was slightly degraded, but still usable, at this operating condition.

Test series 6/4 involved, for the most part, kiln operation without secondary air. In this operating configuration, all the combustion air is supplied through the primary circuit which is in close proximity to the oil flow. This would have the effect of increasing the mixing between these streams and promoting NO production.

Figure 3-2 presents these data in terms of NO vs. O₂. Test 6/4-4 at 1.3 percent O₂ produced an unacceptably high CO concentration of 2165 ppm (dry, at 3 percent O₂). The balance of these tests show an NO sensitivity of 49.9 ppm/% O₂, however, a comparison with Figure 3-1 shows that operation without secondary air caused an increase in NO for the same O₂ (total air flow).

The original oil tip had seven holes each of which was 5.79 mm (0.228 in.) in diameter, located on a 34.9 mm (1.375 in.) bolt circle diameter and inclined at 35° from the oil gun axis. A new tip was designed, fabricated and installed with the same oil flow area but with only four holes. The new tip was designed to delay mixing between the oil spray and combustion air and thereby reduce the NO emissions.

However, the initial testing of this tip resulted in the oil spray impinging on the kiln insulation in four locations. In addition, the NO emissions increased by 23 percent (test 6/6-1 vs. test 6/5-1). Testing with the new oil tip had to be suspended because of the concern for potential insulation degradation. The tests that were conducted had to be made with a lower fuel oil input.

In summary, the tests performed on the rotary lime kiln showed that lower excess air had a practical limit in reducing NO, i.e., to the point where lime quality was effected. This limitation corresponded to an NO reduction on the order of 23 percent.

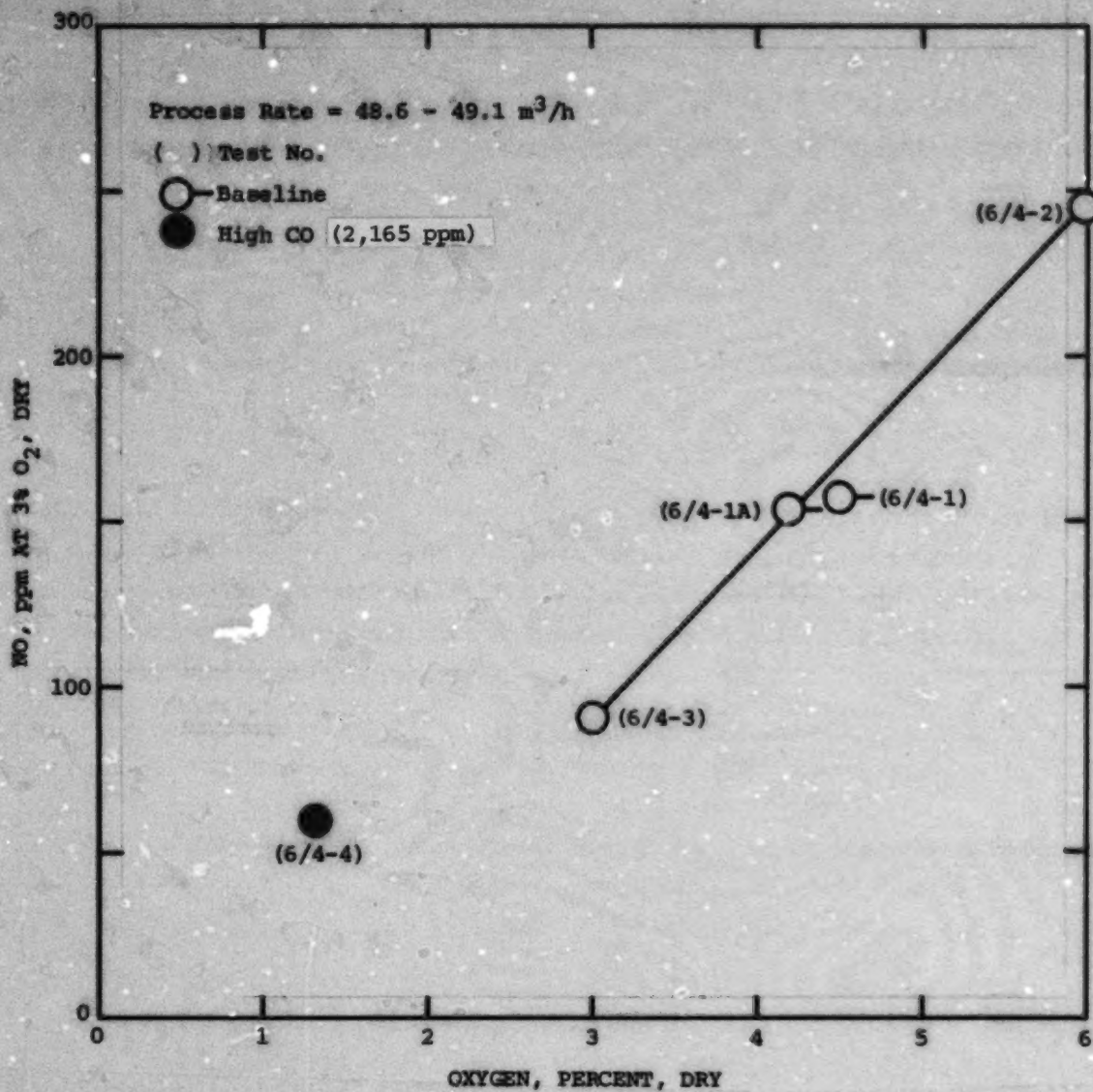


Figure 3-2. Variation of NO with Kiln Exit Oxygen - without Secondary Air, Location 6 Lime Kiln

SECTION 4.0

ROTARY PRECALCINER CEMENT KILN - LOCATION 8

As-found tests were conducted at three locations on a coal-fired precalciner cement kiln. Figure 4-1 is a flow schematic of the basic components of the precalciner kiln. The function of cyclone stages 1, 2 and 3 is to dry and partially calcine the feed prior to the coal-fired flash furnace. It is claimed (Reference 4) that the flash furnace can complete up to 95 percent of the calcination. The fourth cyclone stage separates the feed from the gas stream and discharges the feed into the coal-fired rotary kiln for clinkering. The exhaust gases from the kiln and flash furnace pass through the first three cyclone stages, the crusher/dryer, and the crusher/dryer baghouse before venting to the atmosphere. A portion of the exhaust gases are used in the indirect coal mill, probably for coal drying.

There are four air streams exiting the clinker cooler shown in Figure 4-1. These are the kiln primary and secondary combustion air, flash furnace combustion air and excess air (vented to the atmosphere through the cooler dust collector). The kiln secondary combustion air flows through the freshly discharged clinker (1478-1589 K; 2200-2400°F) and, therefore, will be heated to the highest temperature (approximately 950 K, 1250°F).

The rotary kiln portion of the system is 50 m (165 ft) long and 3.7 m (12 ft) in outside diameter. The kiln length is about one-third that of a conventional kiln.

Testing was performed at the stack* (downstream of the crusher/dryer baghouse and the alkali bypass baghouse), kiln outlet (between kiln and flash furnace) and flash furnace outlet (between flash furnace and fourth cyclone stage). Testing at the stack (downstream of both baghouses) would yield

*The system has just one stack. The discharge streams from both the crusher/dryer baghouse and the alkali bypass baghouse are accommodated by the single stack. Measurements made at the stack were downstream of both discharge streams.

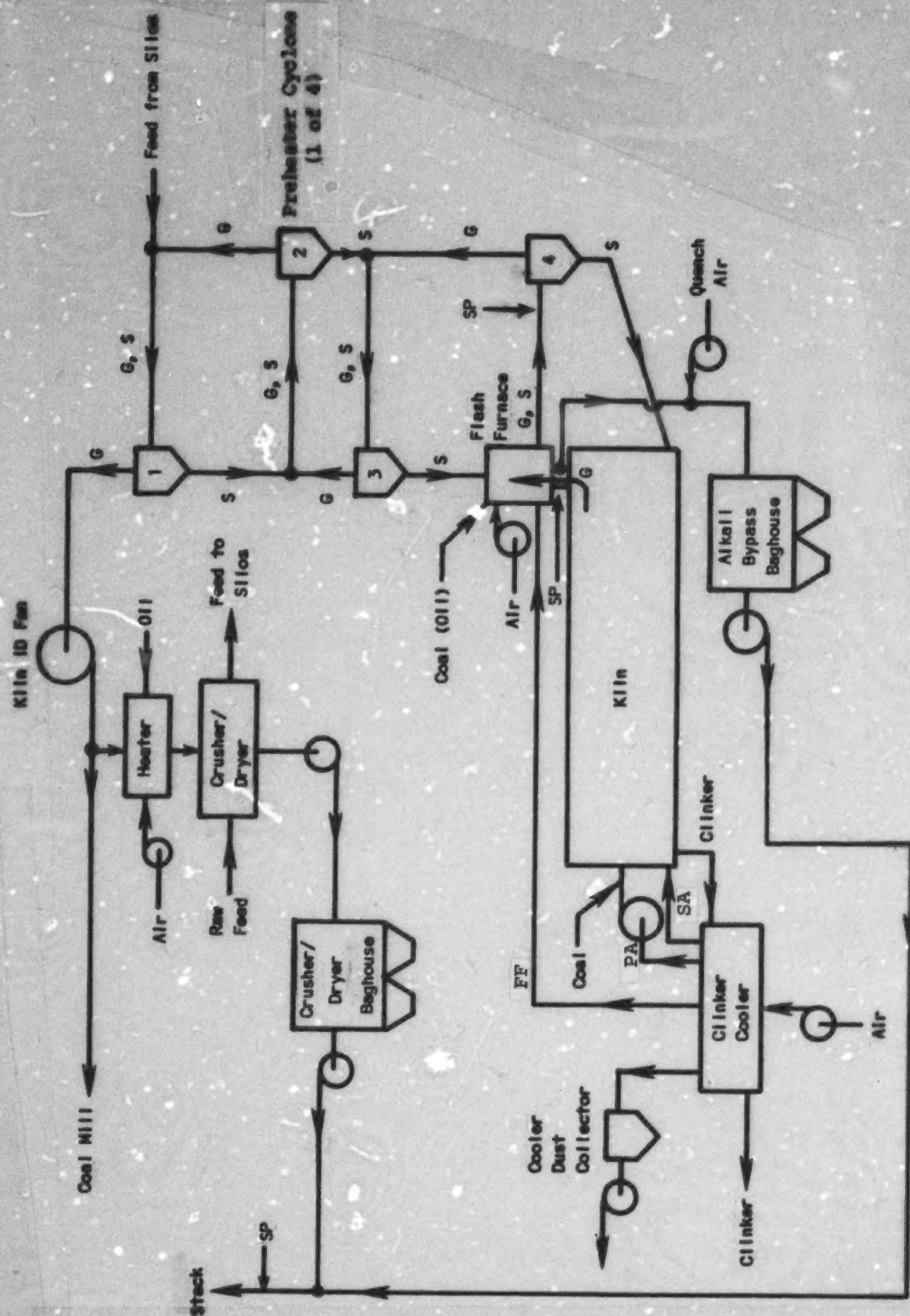


Figure 4-1. Precalciner Kiln Arrangement (G = Gas, S = Solid, SP = Sample Point, PA = Primary Air, SA = Secondary Air, FF = Flash Furnace Air)

measurements of emissions produced by the entire kiln system, while sampling at the kiln outlet and the flash furnace outlet would quantify the emissions produced sequentially within the system.

The test results summarized in Table 4-1 indicate that the stack value of NO ranged from 1173 ppm to 1371 ppm (dry, corrected to 3 percent O₂) while the O₂ was about 13.3 percent. The high value of O₂ is probably due to the quench (tempering) ambient air added upstream of the alkali bypass baghouse. The majority of the flow from the Stage 1 cyclone outlet is used to partially dry the crushed feed. An oil-fired heater is used in the event that the temperature of this flow is too low to accomplish the required feed drying. This heater is probably intermittent in operation. Measurements were not made on the crusher/dryer heater air or fuel flows. However, it is anticipated that these would be minor in comparison to either the kiln-flash furnace flow or alkali bypass flow.

The average "as found" stack NO (1264 ppm, dry at 3 percent excess oxygen) for this site was somewhat higher than the 1000 ppm level from a dry process kiln operating at 2 percent oxygen and considerably lower than the 2500 ppm emission from a wet process kiln operating at 6 percent oxygen (Reference 1). These earlier measurements on the conventional kilns were made at the kiln exit upstream of any pollution control equipment. By comparison, the NO concentration measured at the kiln exit for the precalciner was 912 ppm at an operating O₂ of 5.8 percent. However, even this comparison is not strictly valid due to the operating differences between the rotary kiln portion of a precalciner system and a conventional rotary kiln.

Only the oxygen content of the flash furnace outlet was measured (with a portable oxygen analyzer) since the previous measurement at the high temperature kiln exit had destroyed the sample probe. The test data, however, suggests that the flash furnace is a potential major NO_x source in the system. This was determined by comparing the NO_x emission factors (ng/J) at the kiln outlet and stack for test 8/1-1P, and assuming that the kiln consumed 40 percent of the total heat input. (Reference 4 indicates that the flash

TABLE 4-1. EMISSIONS DATA SUMMARY - PRECALCINER CEMENT KILN LOCATION 8

Test No.	Date	Kiln Feed Rate		O ₂ %	CO ₂ %	NO _x ppm ¹	MO ₄ mg/j ²	CO ppm ¹	SO ₂ ppm	Solid Particulate		Total Particulate lb/10 ⁶ Btu ³	mg/j ²	Probe Location	Comments
		kg/a	(t/h)							lb/10 ⁶ Btu ³	mg/j ²				
8/1-1	8-6	24.1	(95.4)	13.5	12.8	1371	1,054	241	51	--	--	--	--	Stack	As Found, gaseous emissions
8/1-1P	8-7	26.5	(105)	13.4	13.7	1249	960	355	0	0.0086	30.1	0.1434	61.7	Stack	As Found, particulates
8/1-1P	8-7	26.5	(105)	5.8	20.0	912	543 ³	12	0	--	--	--	--	Kiln Outlet	As Found
8/1-1G	8-8	28.8	(114)	13.1	15.0	1173	902	365	24	--	--	--	--	Stack	As Found
8/1-1A	8-8	28.8	(114)	8.5	--	--	--	--	--	--	--	--	--	Flash Pos. Out.	As Found, excess O ₂ at flash furnace outlet

¹dry, corrected to 3% O₂.

²dry, corrected to 3% O₂, corrected for CO₂ generation in the kiln and precalciner.

³dry, corrected to 3% O₂, corrected for CO₂ generation in the kiln only.

⁴NO_x as NO₂.

furnace utilizes 50-70 percent of the total fuel burned.) This analysis indicates that the kiln outlet NO_x , on a mass rate basis, is only 23 percent of the stack NO .

As noted in Figure 4-1, the only other combustion source of NO downstream of the flash furnace is the oil-fired crusher/dryer heater. Data supplied by the plant indicated that this heater was "on" during test 8/1-1P, however, the heater rating (and its potential NO production) was not obtained. Nonetheless, the possibility exists that the flash furnace is responsible for a significant percentage of the NO mass emission rate.

Table 4-2 presents the various operating temperatures as measured by the plant during the test program. As noted, the kiln outlet temperature is 160-230 K (285-414°F) higher than the flash furnace outlet with this difference increasing with increasing feed rate.

The total particulate measured after the baghouses was 61.7 ng/J, and the solid particulate had a log-normal size distribution as shown in Figure 4-2, with a geometric mean of approximately 6 μm . By comparison, the wet conventional kiln previously tested (Reference 1) had a total particulate emission factor after an ESP of 26.1 ng/J. The solid particulate was also log-normally distributed with a geometric mean of 8 μm . (The ESP had a 99.59 percent collection efficiency for total particulate, however, the collection efficiencies of the precalciner baghouses were not determined.)

Coal samples were obtained and analyzed during the test program with the results presented in Table 4-3. This coal is ranked, according to ANSI/ASTM D 388-77, as a high volatile "A" bituminous coal. Of note is that even though the coal sulfur content ranged from 1.9 to 2.1 percent the measured SO_2 concentration did not exceed 51 ppm (dry, corrected to 3 percent O_2). Also, the fuel nitrogen content (1.34 to 1.62 percent) may be a factor in the relatively high NO emissions from the precalciner kiln.

The kiln had been placed in service shortly before the test program and it is possible that its operation had not yet been fully optimized.

TABLE 4-2. LOCATION 8 PRECALCINER KILN OPERATING TEMPERATURES

K/°F

	Test		
	<u>8/1-1</u>	<u>8/1-1P</u>	<u>8/1-1G, 8/1-1A</u>
Combustion Air			
Kiln Primary	378/220	378/220	377/219
Kiln Secondary	926/1207	953/1255	972/1290
Kiln Outlet	1283/1850	1312/1902	1356/1980
Flash Furnace Outlet	1125/1565	1131/1576	1126/1566
Stage 4 Outlet	1101/1521	1100/1520	1100/1520
Stage 3 Outlet	1038/1408	1039/1411	1029/1393
Stage 2 Outlet	918/1193	906/1170	893/1148
Stage 1 Outlet	624/664	634/681	644/699
Crusher/Dryer Baghouse Inlet	492/425	486/414	505/449
Alkali Bypass Baghouse Inlet	428/311	413/284	412/281

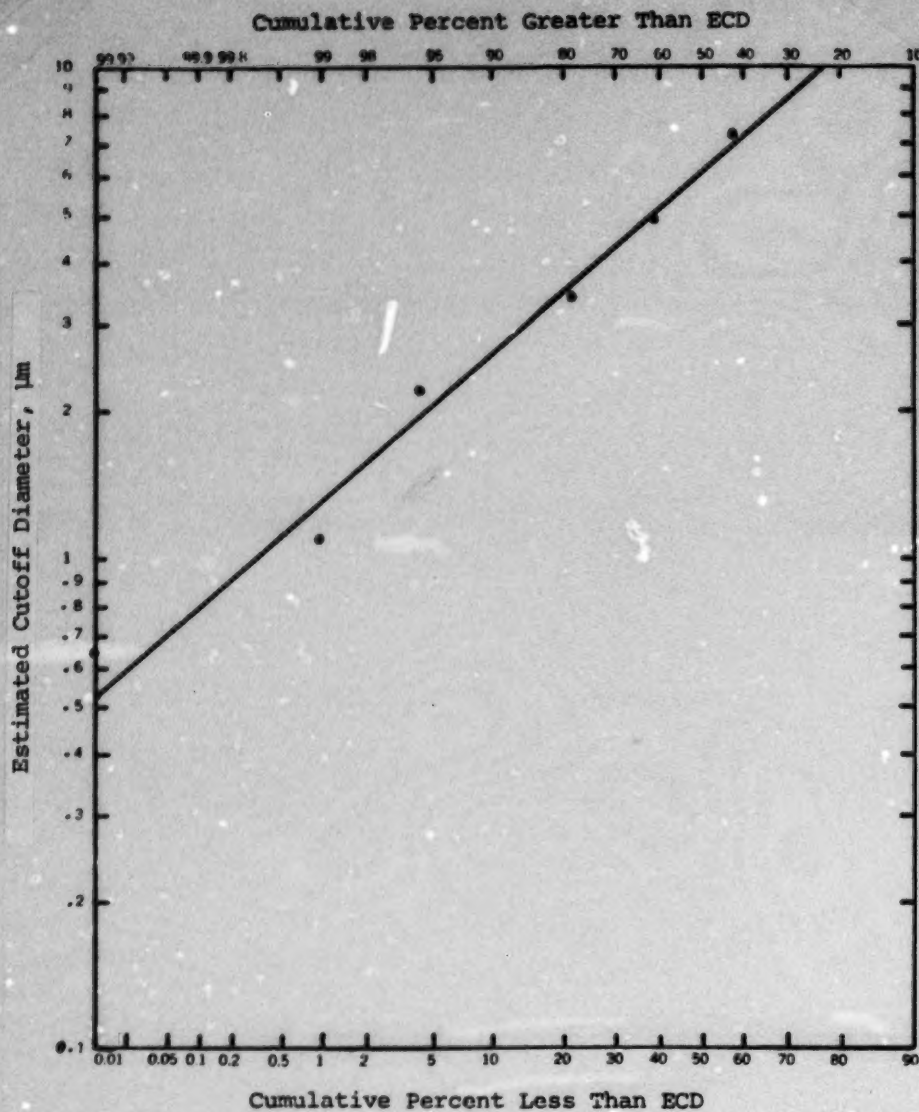


Figure 4-2. Estimated cutoff diameter (ECD) as a function of the cumulative weight percent of the sample less than the ECD for Location 8 precalciner cement kiln firing coal.

TABLE 4-3. COAL FUEL ANALYSES FOR LOCATION 8

Test 8/1-1
August 6, 1980

PROXIMATE ANALYSIS

	<u>As Rec'd.</u>	<u>Dry Basis</u>
%Moisture	2.16	xxxxx
%Ash	12.78	13.06
%Volatile	33.82	34.57
%Fixed Carbon	51.24	52.37
	<u>100.00</u>	<u>100.00</u>
Btu/lb.	12491	12767
%Sulfur	1.90	1.94

ULTIMATE ANALYSIS

	<u>As Rec'd</u>	<u>Dry Basis</u>
%Moisture	2.16	xxxxx
%Carbon	69.77	71.31
%Hydrogen	4.82	4.93
%Nitrogen	1.62	1.66
%Chlorine	0.04	0.04
%Sulfur	1.90	1.94
%Ash	12.78	13.06
%Oxygen(diff)	6.91	7.06
	<u>100.00</u>	<u>100.00</u>

Test 8/1-1P
August 7, 1980

PROXIMATE ANALYSIS

	<u>As Rec'd.</u>	<u>Dry Basis</u>
%Moisture	2.14	xxxxx
%Ash	10.80	11.04
%Volatile	34.75	35.51
%Fixed Carbon	52.31	53.45
	<u>100.00</u>	<u>100.00</u>
Btu/lb.	12878	13160
%Sulfur	1.90	1.94

ULTIMATE ANALYSIS

	<u>As Rec'd</u>	<u>Dry Basis</u>
%Moisture	2.14	xxxxx
%Carbon	71.45	73.01
%Hydrogen	4.89	5.00
%Nitrogen	1.57	1.60
%Chlorine	0.04	0.04
%Sulfur	1.90	1.94
%Ash	10.80	11.04
%Oxygen(diff)	7.21	7.37
	<u>100.00</u>	<u>100.00</u>

Tests 8/1-1G and 8/1-1A
August 8, 1980

PROXIMATE ANALYSIS

	<u>As Rec'd.</u>	<u>Dry Basis</u>
%Moisture	2.05	xxxxx
%Ash	12.54	12.80
%Volatile	34.39	35.11
%Fixed Carbon	51.02	52.09
	<u>100.00</u>	<u>100.00</u>
Btu/lb.	12662	12927
%Sulfur	2.09	2.13

ULTIMATE ANALYSIS

	<u>As Rec'd</u>	<u>Dry Basis</u>
%Moisture	2.05	xxxxx
%Carbon	70.45	71.92
%Hydrogen	4.88	4.98
%Nitrogen	1.34	1.37
%Chlorine	0.04	0.04
%Sulfur	2.09	2.13
%Ash	12.54	12.80
%Oxygen(diff)	6.61	6.76
	<u>100.00</u>	<u>100.00</u>

Samples were obtained of the raw feed, clinker, alkali by-pass baghouse catch and crusher/dryer baghouse catch, for the purpose of performing mass balances for sulfur, sodium and potassium.

The sample analyses, performed by the plant, presented in Table 4-4 together with the coal analyses (Table 4-3) and process weights were analyzed by a contractor retained by the plant owner. The sodium and potassium concentrations were determined by atomic absorption; chlorine by titration with silver nitrate; sulfur by the Leco furnace technique. These determinations, as well as the ignition loss, are in accordance with ASTM C-114. Nitrogen determinations, performed by an outside laboratory, were by the Kjeldahl Comprehensive Nitrogen Test. This element is not covered by ASTM C-114. The results of the mass balances are shown in Table 4-5. Of note is the high degree of closure on all three mass balances.

The fossil-fuel energy required to produce the clinker averaged about 3.3×10^6 Btu/ton clinker (3838 kJ/kg clinker). This heat rate is nearly 32 percent less than the average for preheater kilns (4.8×10^6 Btu/ton -- 5582 kJ/kg) determined during a 1973 survey conducted by the Portland Cement Association (Reference 4).*

*The 1973 survey did not specifically enumerate the energy requirement for precalciner systems. The value of 5582 kJ/kg may be applicable only to grate or suspension preheater installations.

TABLE 4-4. SUMMARY OF MATERIAL ANALYSES - LOCATION 8
Weight Percent

PROCESS MATERIALS						
Date	Parameter	Waste Dust from By-Pass	Return Dust from Baghouse	Kiln Feed	Discharge of Stage IV	Clinker
8/6/80	SO ₃ (total)	7.9		0.48	2.5	1.2
	Na ₂ O	0.34		0.12	0.22	0.20
	K ₂ O	5.6		0.64	1.8	0.92
	Cl	1.03		0.026	0.18	<0.001
	N (total)	0.0047			0.0058	0.0039
	Loss	6.8		35.2	7.0	0.04
8/7/80	SO ₃ (total)	6.7	0.91	0.38	2.2	0.89
	Na ₂ O	0.25	0.10	0.09	0.17	0.14
	K ₂ O	4.6	0.92	0.62	1.8	0.76
	Cl	0.38	0.10	0.022	0.19	<0.001
	N (total)	0.0041	0.0200	0.0190	0.0044	0.0063
	Loss	5.7	32.5	35.3	10.4	0.38
8/8/80	SO ₃ (total)	3.6		0.40	1.8	0.94
	Na ₂ O	0.27		0.15	0.25	0.23
	K ₂ O	2.9		0.59	1.4	0.80
	Cl	0.75		0.021	0.17	0.002
	N (total)	0.0039		0.0108	0.0044	0.0012
	Loss (Gain)	9.3		35.0	7.7	(0.09)

TABLE 4-5. MASS BALANCES FOR PRECALCINER CEMENT KILN - LOCATION 8

Element		Input lb/hr (kg/hr)			Output lb/hr (kg/hr)		Output/Input
Sulfur	Coal	324	(147)	Clinker ¹	484	(220)	
	Raw Feed	<u>319</u>	<u>(145)</u>	Alkali By-Pass Baghouse ²	27	(12.3)	
		643	(292)	Crusher/Dryer Baghouse ³	87	(39.5)	
				SO ₂ in stack	<u>0</u>	<u>(0)</u>	
					598	(272)	0.93
Sodium	Coal	0	(0)	Clinker ¹	141	(64.0)	
	Raw Feed	<u>139</u>	<u>(63.1)</u>	Alkali By-Pass Baghouse ²	2	(0.9)	
		139	(63.1)	Crusher/Dryer Baghouse ³	<u>18</u>	<u>(8.2)</u>	
					161	(73.1)	1.16
Potassium	Coal	0	(0)	Clinker ¹	859	(390)	
	Raw Feed	<u>1081</u>	<u>(490)</u>	Alkali By-Pass Baghouse ²	38	(17)	
		1081	(490)	Crusher/Dryer Baghouse ³	<u>183</u>	<u>(83)</u>	
					1080	(490)	1.00

¹Assumed clinker production = 0.65 of raw feed to preheater.

²Based on 0.5 ton/hr (454 kg/hr) of waste dust from alkali by-pass baghouse.

³Based on 12 ton/hr (10,886 kg/hr) of return dust from crusher/dryer baghouse.

SECTION 5.0

ROTARY WET CEMENT KILN - LOCATION 9

This coal-fired wet process kiln is 127 m (415 ft.) long and 3.7 m (12 ft.) in diameter. Figure 5-1 is a sketch of a conventional process kiln. All testing was performed with the sample line located between the kiln exit and the electrostatic precipitator (ESP).

Testing was conducted at each of three conditions:

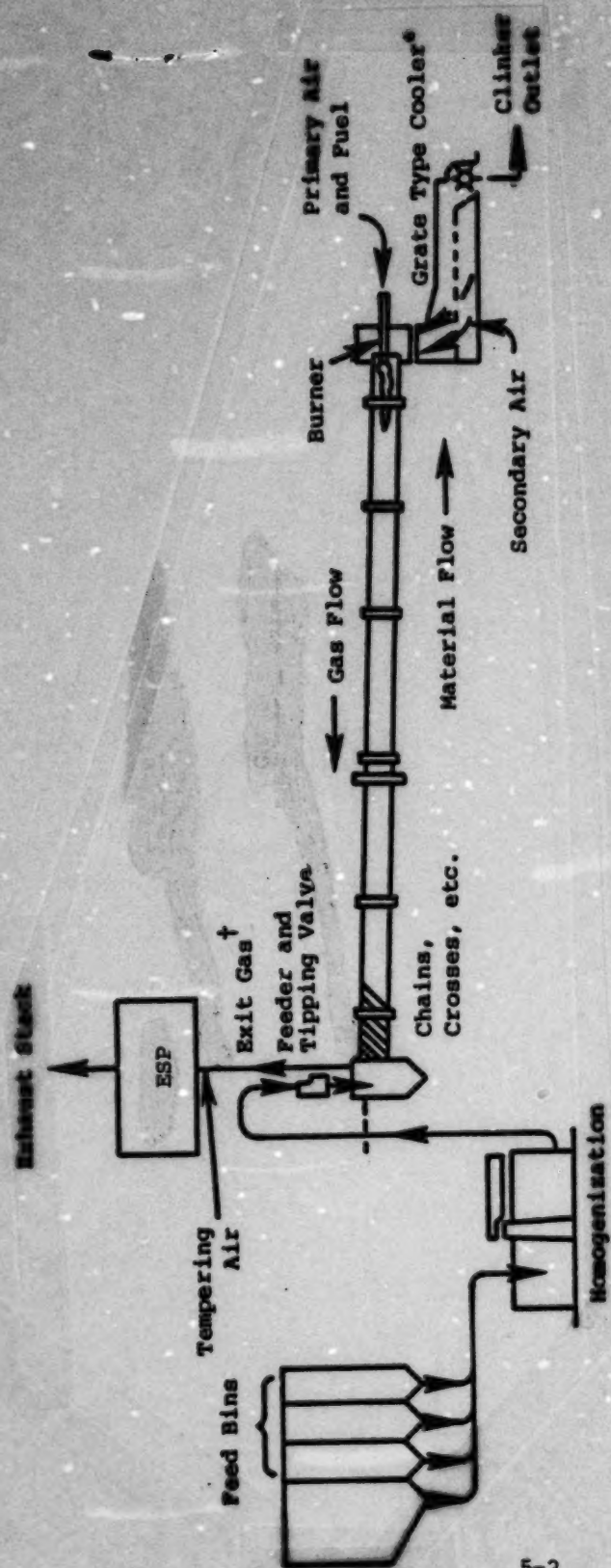
1. As found -- kiln operating under normal conditions with no attempt to control oxygen.
2. Baseline -- oxygen level maintained at nominal value.
3. Oxygen variation -- intentional variations in oxygen level.

Table 5-1 presents the kiln operating conditions (clinker rate and fuel input) and measured gaseous emissions.* Figure 5-2 is a plot of NO_x versus oxygen for all the data except those measured under kiln start-up conditions (tests 9-26 through 9-28). Also shown in this figure are the results of a linear regression between NO_x and O_2 , i.e.:

$$\text{NO}_x \text{ (ppm)} = a + b (\% \text{O}_2)$$

This relationship was able to explain 39.9 percent of the data scatter (a rather weak, but still positive correlation) with the balance (60.1 percent) being due to other than the oxygen variation. Normal variations in the coal nitrogen content could also have a significant effect on NO_x emissions. Quantification of this effect would require, at least, an extensive coal sampling and analysis effort. In addition, the "burnability" of the feed (a measure of the clinker forming reactions), as determined from a detailed feed analysis, influences the temperature within the kiln and, therefore, the NO_x

*The column headed "Input MW" represents the fuel thermal energy input to the kiln. The appropriate conversion is: $\text{MW} = 0.293 \times 10^6 \text{ Btu/hr.}$



5-2

*Cooling air not used for secondary air is exhausted through pollution control device to atmosphere.

†Exhaust gases pass through pollution control device to atmosphere.

Figure 5-1. Schematic of a conventional process cement kiln.

TABLE 5-1. SUMMARY OF GASEOUS EMISSIONS FROM A WET PROCESS ROTARY KILN - LOCATION 9

Test No.	Time	Date 1980	Clinker Rate kg/s	Input MW	O ₂ (%)	CO ₂ (%)	NO _x (ppm)	NO (ppm)	CO (ppm)	SO ₂ (ppm)	Comments
9-1	11:30	8-19	7.66	—	2.8	>20	199	195	129	528	As Found
9-2	12:30	8-19	7.66	—	2.5		185	182	126	924	As Found
9-3	15:30	8-19	7.66	—	1.5		179	175	108	1,624	As Found
9-4	16:00	8-19	7.66	—	2.0		155	149	161	1,934	As Found
9-5	16:30	8-19	7.66	—	1.5		183	171	120	1,691	As Found
9-6	10:00	8-20	7.76	60.5	2.8		186	183	168	2,033	As Found
9-7	11:00	8-20	7.76	60.5	2.8		—	173	188	—	As Found
9-8	12:00	8-20	7.76	60.5	3.0		166	165	175	1,207	As Found
9-9	13:00	8-20	7.76	60.5	2.8		190	188	188	1,542	As Found
9-10	14:00	8-20	7.76	60.5	2.6		158	154	166	1,773	As Found
9-11	15:00	8-20	7.76	60.5	3.1		156	151	191	1,652	As Found
9-12	16:00	8-20	7.76	60.5	2.8		157	143	184	1,368	As Found
9-13	17:00	8-20	7.76	60.5	2.9		154	152	143	1,727	As Found
9-14	18:00	8-20	7.76	60.5	3.1		143	140	191	1,288	As Found
9-15	10:30	8-21	7.99	54.4	2.9		192	185	189	1,577	Baseline
9-16	11:00	8-21	7.99	54.4	2.9		180	175	179	1,083	Baseline
9-17	11:30	8-21	7.99	54.4	2.7		179	179	167	1,738	Baseline
9-18	12:00	8-21	7.99	54.4	2.9		198	191	159	1,865	Baseline
9-19	13:30	8-21	7.99	54.4	3.6		200	193	151	754	O ₂ Variation
9-20	14:00	8-21	7.99	54.4	4.1		208	199	155	815	O ₂ Variation
9-21	14:30	8-21	7.99	54.4	4.0		207	196	169	712	O ₂ Variation
9-22	15:00	8-21	7.99	54.4	3.9		223	218	154	467	O ₂ Variation
9-23	15:30	8-21	7.99	54.4	3.9		206	195	168	881	O ₂ Variation
9-24	16:00	8-21	7.99	54.4	4.6		279	269	159	244	O ₂ Variation
9-25	16:30	8-21	7.99	54.4	2.5		136	126	296	788	O ₂ Variation
9-26	7:30	8-23	—	—	1.2		224	214	116	1,213	Kiln under start-up
9-27	7:45	8-23	—	—	0.9	>20	201	197	1,791	>2,000	Kiln under start-up
9-28	8:00	8-23	—	—	1.2	19.8	325	318	145	982	Kiln under start-up

NO_x, NO, CO and SO₂ corrected to 3%O₂, dry.NO_x (ng/J) = NO_x (ppm) • 0.654, includes CO₂ generation in kiln.

NO (ng/J) = NO (ppm) • 0.654.

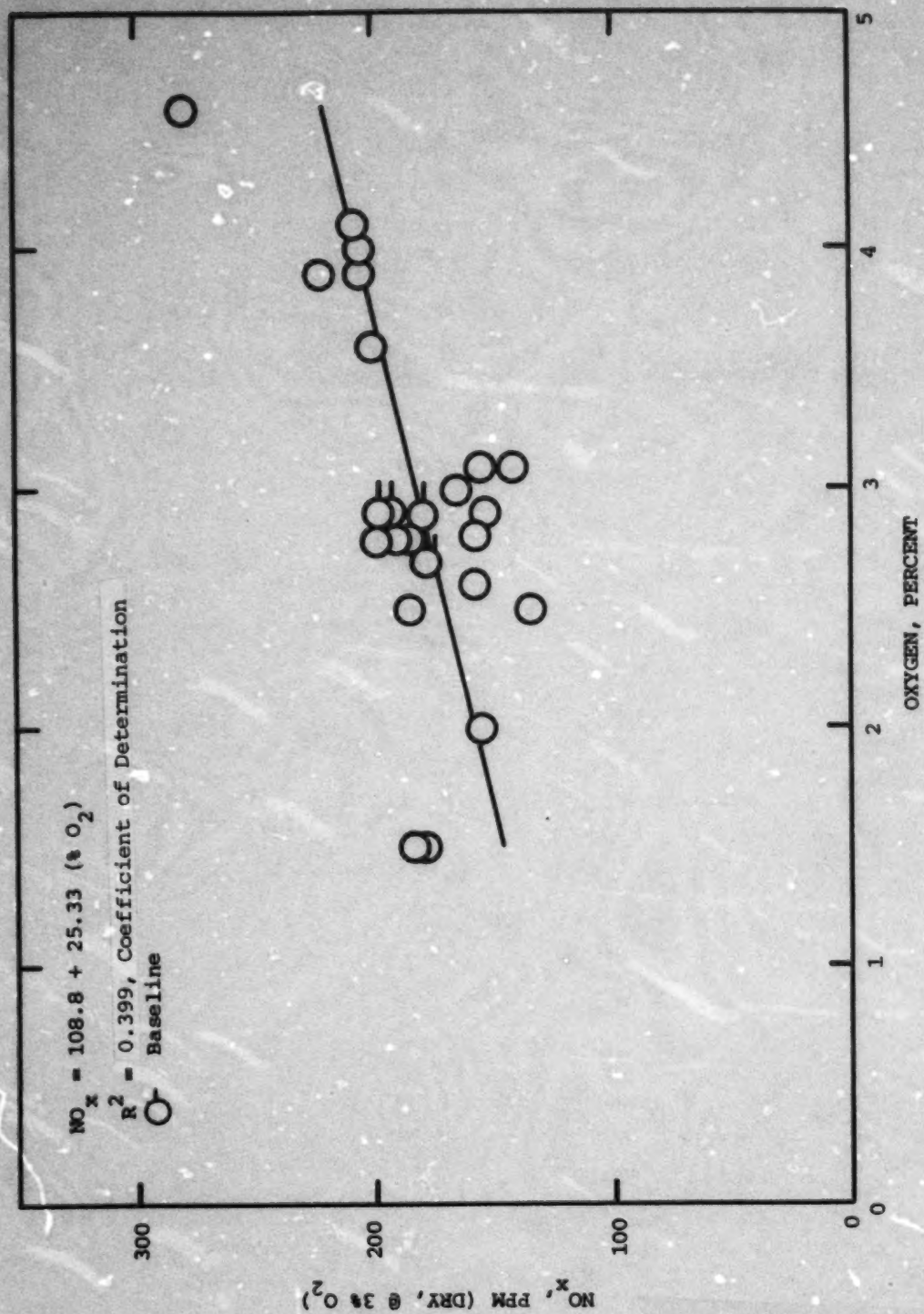


Figure 5-2. Variation of NO_x with Kiln Exit Oxygen, Location 9 Wet Process Cement Kiln

emissions. Based on the linear regression a NO_x reduction of 38 percent is predicted when the oxygen level is lowered from 2.9 percent (baseline average) to 1.5 percent.

Similarly, Figure 5-3 depicts the effect of oxygen on SO_2 emissions. The linear regression between SO_2 and O_2 is also noted and shows a decrease in SO_2 with an increase in O_2 . Also, the linear regression shows that the variation in O_2 explains 43.6 percent of the variation in SO_2 . This relationship predicts a 46.6 percent increase in SO_2 concentration if the operating O_2 is reduced from 2.85 percent (baseline average) to 1.5 percent.

Normal variations in coal and feed sulfur contents could have a significant effect on kiln SO_2 emissions. As was discussed for NO_x vs. O_2 , quantification of this effect would require an extensive program involving the analysis of many fuel and feed samples and their relationship to the measured SO_2 concentration.

Normal variations in process operation (e.g., burning zone temperature, feed composition and fuel properties) can also affect both the NO_x and SO_2 emissions. Indeed, a linear regression performed on the NO_x and O_2 data measured during a three-hour time period on the same day (Tests 9-19 through 9-25) was able to explain 88.4 percent of the NO_x data scatter. This regression conducted with data obtained over a short period of time, when compared with the regression of all the data, illustrates that normal variations in feed and fuel properties and kiln conditions can affect the long-term relationships between NO_x , SO_2 , and oxygen.

The purpose of developing the linear regressions for NO_x and SO_2 was to determine the extent to which they were related to a single independent variable, namely O_2 . It was recognized that this procedure would not consider the effects of other potentially significant variables. In combustion devices where there is direct contact between the combustion products and the feed, there is some degree of interaction between the streams such that a regression in terms of multiple independent variables would be necessary to more completely describe the measured pollutant concentrations in terms of operational conditions.

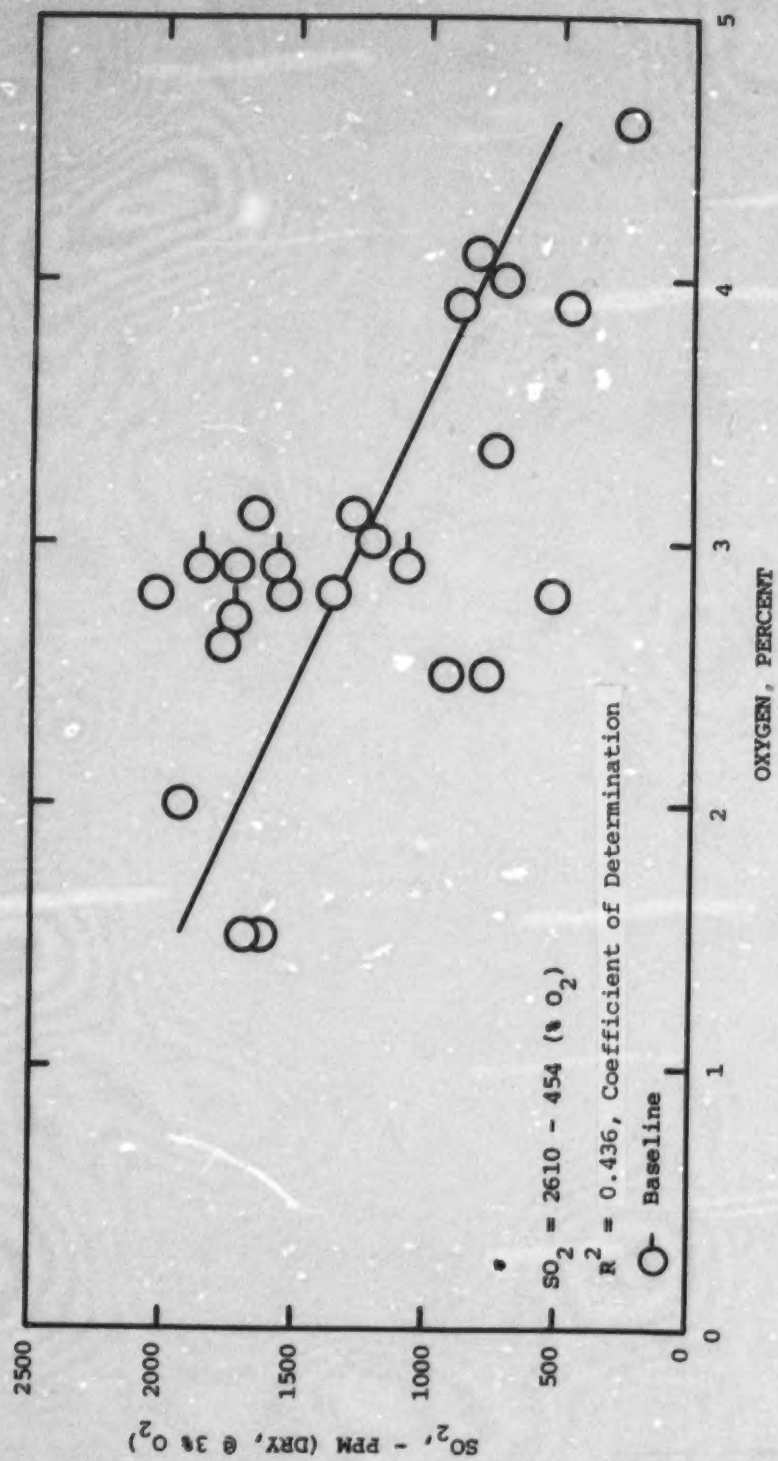
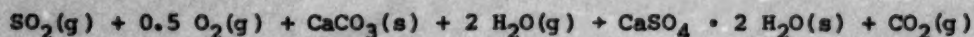


Figure 5-3. Variation of SO₂ with Kiln Exit Oxygen, Location 9 Wet Process Cement Kiln

The SO₂ dependence suggests a reaction between SO₂ and feed alkali components in the presence of oxygen. Laboratory and full-scale tests (Reference 5) have also shown that water vapor speeds up the reaction between SO₂ and alkali. In this respect the feed is performing as a flue gas desulfurization agent (Reference 6), i.e.:



where

g = gas

s = solid

The above global reaction indicates that both oxygen and water vapor are required for the reaction between SO₂ and limestone (or lime).

Triplicate particulate runs were performed upstream of the ESP during tests 9-1, 9-4 and 9-18. The solid particulate results were 10,062, 11,318 and 12,023 ng/J (23.40, 26.32 and 27.96 lb/10⁶ Btu). No particulate measurements were made downstream of the ESP.

On August 20, 1980, hourly samples were obtained of coal, kiln feed, clinker and precipitator catch for the express purpose of performing constituent mass balances. The sample analysis results are shown in Tables 5-2 and 5-3. (An oxide analysis of the coal ash was not performed.) X-ray fluorescence (XRF) was used by the plant for the elemental analyses. The procedures contained in ASTM C-114 were followed including equipment certification with NBS standards. In addition, a single coal sample was analyzed on both a proximate and ultimate basis (Table 5-4). As noted from Table 5-2 the coal fuel was the only source of sulfur since none was measured in the dry feed.

In addition to the coal consumption rate and clinker production rate, the precipitator catch was also measured. Not measured, however, was the kiln feed rate. This quantity was estimated on the basis that 1.67 kg of dry feed is required to produce 1 kg of clinker. This value was taken from previous tests on a natural gas-fired wet kiln (Reference 1) and includes the evolution of CO₂ gas and entrainment of a portion of the feed by the combustion

TABLE 5-2. KILN MATERIAL ANALYSIS FOR WET PROCESS CEMENT KILN -
LOCATION 9

	Weight Percent (Standard Deviation)		
	<u>Dry Feed</u>	<u>Clinker</u>	<u>Precipitator Dust</u>
SiO ₂	13.46 (0.12)	20.44 (0.20)	15.27 (0.70)
Al ₂ O ₃	3.45 (0.13)	5.90 (0.14)	4.63 (0.27)
Fe ₂ O ₃	1.89 (0.14)	4.10 (0.17)	1.78 (0.11)
CaO	41.82 (0.28)	64.19 (0.23)	36.06 (1.73)
MgO	2.26 (0.14)	3.65 (0.19)	2.59 (0.19)
SO ₃	0	0.23 (0.09)	8.08 (0.31)
K ₂ O	0.53 (0.01)	0.57 (0.12)	2.81 (0.47)
TiO ₂	0	0.27 (0.02)	0
Mn ₃ O ₄	0	0.02 (0.01)	0
P ₂ O ₅	0	0.01 (0.01)	0
Ignition Loss*	36.43 (0.10)	0	21.93 (1.05)
Total	99.84	99.38	93.15

*Weight loss due to carbonate decomposition.

TABLE 5-3. COAL PROXIMATE ANALYSES FOR WET PROCESS CEMENT KILN -
LOCATION 9

Average (Standard Deviation)

Volatiles*	37.7 (0.59)
Ash*	16.3 (3.60)
Fixed Carbon*	42.8 (3.74)
Sulfur*	3.27 (0.21)
Btu/lb	11,917 (107)
kJ/kg	27,719 (249)

*Weight percent, dry basis

TABLE 5-4. COAL FUEL ANALYSIS FOR LOCATION 9 NET PROCESS CEMENT KILN

TEST 9-3

Proximate Analysis			Ultimate Analysis		
	As Rec'd.	Dry Basis		As Rec'd.	Dry Basis
%Moisture	2.38	xxxxx	%Moisture	2.38	xxxxx
%Ash	13.39	13.72	%Carbon	65.88	67.49
%Volatile	36.08	36.96	%Hydrogen	4.61	4.72
%Fixed Carbon	48.15	49.32	%Nitrogen	1.17	1.20
	100.00	100.00	%Chlorine	0.10	0.10
Btu/lb.	12,004	12,297	%Sulfur	3.43	3.51
KJ/kg	27,921	28,603	%Ash	13.39	13.72
%Sulfur	3.43	3.51	%Oxygen (diff.)	9.04	9.26
				100.00	100.00

products. The oxide analysis of a coal with a similar ash content was used as an input stream in the mass balances.

Mass balances were performed for aluminum, silicon, iron, calcium, magnesium, potassium and sulfur using the measured oxide concentrations in the kiln feed, clinker and precipitator catch. As previously mentioned a coal ash analysis was assumed since none was made on the coal actually used. In addition, the average flue gas SO_2 volume concentration measured during the same time period was converted to an equivalent sulfur outlet stream on a weight basis. The overall approach does not account for particulates passing through the ESP and assumes that the gaseous SO_2 is not converted to other sulfur compounds within the ESP. (With respect to ESP collection efficiency, a previous KVB test on a wet kiln (Reference 1) demonstrated an ESP collection efficiency of 99.59 percent.)

The mass balance results are shown in Table 5-5 for each individual constituent and for all the constituents. As noted, the largest difference was for iron oxide where the outlet streams exceeded the inlet streams by 29.5 percent. Part of this difference could be due to kiln metal material loss which would increase the iron content of the outlet streams (clinker and precipitator catch). Based on the sulfur mass balance it is estimated that the coal sulfur is distributed as follows:

Clinker	10.3%
Precipitator Catch	23.8%
Flue Gas	54.5%
Unaccounted	11.4%

Thus, for this particular kiln only 54.5 percent of the coal sulfur is emitted as SO_2 .

Also noted in Table 5-5 is that the overall mass balance for the seven constituents is within 4 percent.

TABLE 5-5. MASS BALANCES FOR WET PROCESS
CEMENT KILN - LOCATION 9

Constituent	In		Out		% Difference*
	Mg/d	(tons/day)	Mg/d	(tons/day)	
Al ₂ O ₃	40.1	(44.2)	41.4	(45.6)	3.2
SiO ₂	152.1	(167.7)	143.0	(157.6)	-6.0
Fe ₂ O ₃	21.7	(23.9)	28.1	(31.0)	29.5
CaO	468.2	(516.1)	443.9	(489.3)	-5.2
MgO	25.4	(28.0)	25.5	(28.1)	0.4
K ₂ O	5.96	(6.57)	5.03	(5.55)	-15.6
S	<u>5.98</u>	<u>(6.59)</u>	<u>5.30</u>	<u>(5.84)</u>	<u>-11.4</u>
Total	719.4	(793.1)	692.2	(763.0)	-3.8

$$\frac{*(Out-In)}{In} \times 100$$

The kiln heat rate varied from 7897 kJ/kg (6.8×10^6 Btu/ton clinker) to 6812 kJ/kg (5.9×10^6 Btu/ton clinker) during the test program. These values are at or below the average of 7897 kJ/kg (6.8×10^6 Btu/ton clinker) reported for a 1973 survey of wet process kilns (Reference 4).

The stack losses were computed for several of the tests and the results presented below:

<u>Test</u>	<u>O₂, %, dry</u>	<u>Stack Loss, % of Fuel Input</u>
9-18	2.9	11.9
9-19	3.6	12.2
9-20	4.1	12.4
9-24	4.6	12.6
9-25	2.5	11.7

As noted, the stack loss decreases (thermal efficiency increases) as the operating O₂ is reduced.

SECTION 6.0

SUBSCALE CEMENT KILN STUDIES

The objectives of the laboratory program are to identify the mechanisms of NO_x formation in the "near burner" zone within a cement kiln and to determine possible methods for the control of NO_x emissions. The results would provide guidance for the field modification of a pilot-scale unit to demonstrate advanced NO_x control approaches.

6.1 LABORATORY FACILITY

A lab-scale model of a typical cement kiln burner and furnace, capable of firing natural gas or pulverized coal, was constructed in KVB's Combustion Laboratory. The key variables investigated were fuel injection velocity, furnace temperature, preheat temperature, fuel carrier oxygen concentration, and excess air. No product was made by the furnace.

The test furnace is shown in Figure 6-1. By using a different size refractory, the furnace inside diameter can be made either 5 or 8 inches (0.127 or 0.203 m). In addition, refractories of two different thermal conductivities were used to vary the furnace temperature. These insulations were Kaiser Purotab Coarse* (high density, high thermal conductivity, 97 percent alumina) and Kaiser Purolite 30* (low density, low thermal conductivity, 54 percent alumina). At 1500°F (1089 K) the ratio of the thermal conductivities is 2.8. In subsequent discussions these insulations are referred to as "HD" and "LD", respectively. The secondary combustion air is admitted through two concentric annuli. The flow can be biased to one or the other annulus, and it is also possible to preheat one stream and not the other. The fuel carrier can be air or nitrogen, or a combination of the two. Pulverized coal, when fired, is fed to the injection pipe by a Vibrascrew feeder. Figure 6-2 shows the furnace and its ancillary equipment. Flue

*Mention of trade names or products does not constitute endorsement by EPA.

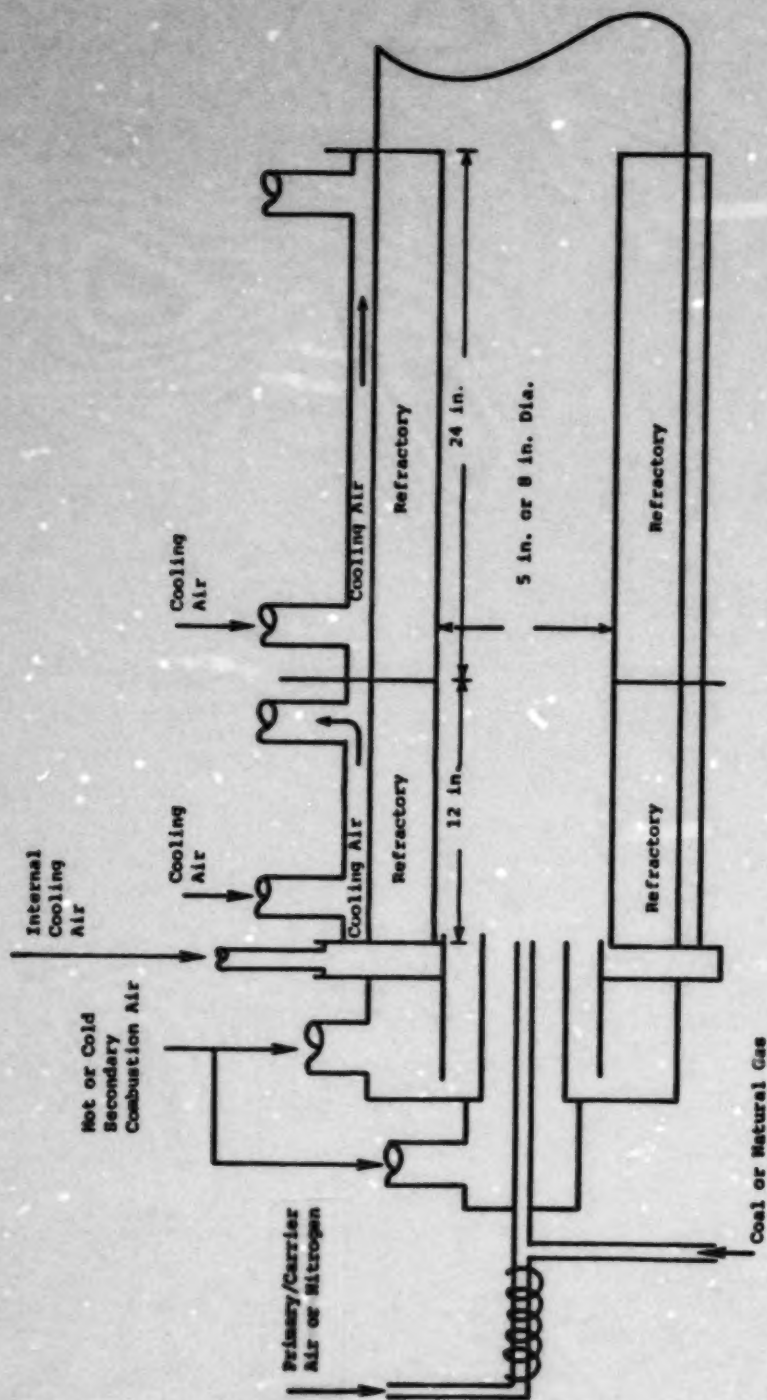


Figure 6-1. Schematic of Subscale Test Furnace

gas is drawn from the stack and fed to continuous NO/NO_x, CO, CO₂, and SO₂ analyzers. Table 6-1 is a listing of the measurement equipment. All mass flows supplied to the furnace were monitored.

The burners used in this program for both fuels were straight sections of pipe of differing diameter. The diameters ranged from 3/16" (4.8 mm) to 1" (25.4 mm) and were used to vary the fuel injection velocity at constant heat input rate.

A combustion preheater was added to the existing test facility. This natural gas-fired preheater is supplied with air at about 900°F (756 K) from the electric heating manifold (shown in Figure 6-2) and increases the combustion air temperature to 1600°F (1144 K). Pure oxygen is added at the discharge to bring the oxygen concentration to 21 percent. The testing capabilities of the cement kiln simulation facility are primarily as follows:

- Fuel - pulverized coal, natural gas
- Combustion air preheat - 80-900°F (300-756 K) (electric preheat) - 1600°F (1144 K) (combustion preheat)
- Fuel injection velocity - 10-900 ft/sec. (3.1-274 m/s)
- Heat input - up to 230,000 Btu/hr (0.07 MW_t)
- Burner surface heat release rate - 660,000 - 1,760,000 Btu/ft²-hr (0.018-0.048 MW_t/m²)

The natural gas injection velocity and coal carrier gas injection velocity were calculated on the basis of their measured mass flow rate, injector area and the assumption of standard temperature and pressure at the injection plane.

Table 6-2 contains two ultimate analyses of the coal used in the program. This coal is classified as a high volatile "A" bituminous. No analysis was made of the natural gas fuel.

6.2 TEST RESULTS

This section will describe the scope of tests completed, the most significant data, and provide a summary of the key variables identified in the laboratory to affect NO_x formation in cement kilns.

TABLE 6-1. ANALYTICAL INSTRUMENTATION EMPLOYED -
LABORATORY TEST FURNACE

Emission Species	Measurement Method	Manufacturer	Model No.
Oxygen	Fuel Cell	Teledyne	720P4
Carbon Dioxide	NDIR	Horiba	PIR2000
Carbon Monoxide	NDIR	Horiba	PIR2000
Nitrogen Oxides	Chemiluminescent	Thermo Electron	10A
Sulfur Dioxide	UV Spectrometer	Du Pont	411

TABLE 6-2. COAL ULTIMATE ANALYSES -
LABORATORY TEST FURNACE

As Received

	<u>Sample 1</u>	<u>Sample 2</u>
Moisture	3.85	3.51
Carbon	71.31	73.54
Hydrogen	4.79	4.88
Nitrogen	1.29	1.18
Chlorine	0.04	0.05
Sulfur	1.01	1.05
Ash	8.97	7.63
Oxygen (diff)	8.74	8.16
Btu/lb	12,698	13,019
kJ/kg	29,536	30,282

Test variables examined during this program included:

- . Combustion air preheat
- . Oxygen concentration in carrier air
- . Furnace wall temperature
- . Furnace heat release rate
- . Fuel injection velocity
- . Furnace O_2

A review of the important results obtained during the program is presented below.

Figure 6-3 presents NO_x as a function of injection velocity for natural gas fuel with air carrier and with N_2 carrier. The data show that NO_x emissions are higher with air carrier than with N_2 carrier. The slope of the NO_x vs. fuel injection velocity curve is also greater with air carrier. This apparently results from the improved fuel/oxidant mixing when oxidant is present in both the fuel jet and the secondary air stream. The flame thus burns oxidant rich, and more O_2 is available to form NO. Another possible factor is the quenching effect of the nitrogen resulting in a reduced combustion temperature.

This effect is also noted for coal fuel as shown in Figure 6-4 which demonstrates the NO_x reduction measured when the carrier (primary) stream oxygen content is reduced by the addition of N_2 . On a full-scale kiln this effect could be implemented by replacing a portion of the carrier air stream with recirculated flue gas products or other inert gas.

Figure 6-5 illustrates the effect of furnace temperature upon NO_x emissions with a pure gas fuel jet, i.e., without primary air. With high-density (high thermal conductivity) refractory and no preheat, NO_x emissions are low and the NO_x vs. injection velocity slope is very small. Preheated combustion air (800-900°F--700-756 K) in the same furnace increases NO_x emissions and the slope. When low density (low thermal conductivity) refractory was used with air preheat, the NO_x and the slope increased further reflecting a more intense and hot combustion.

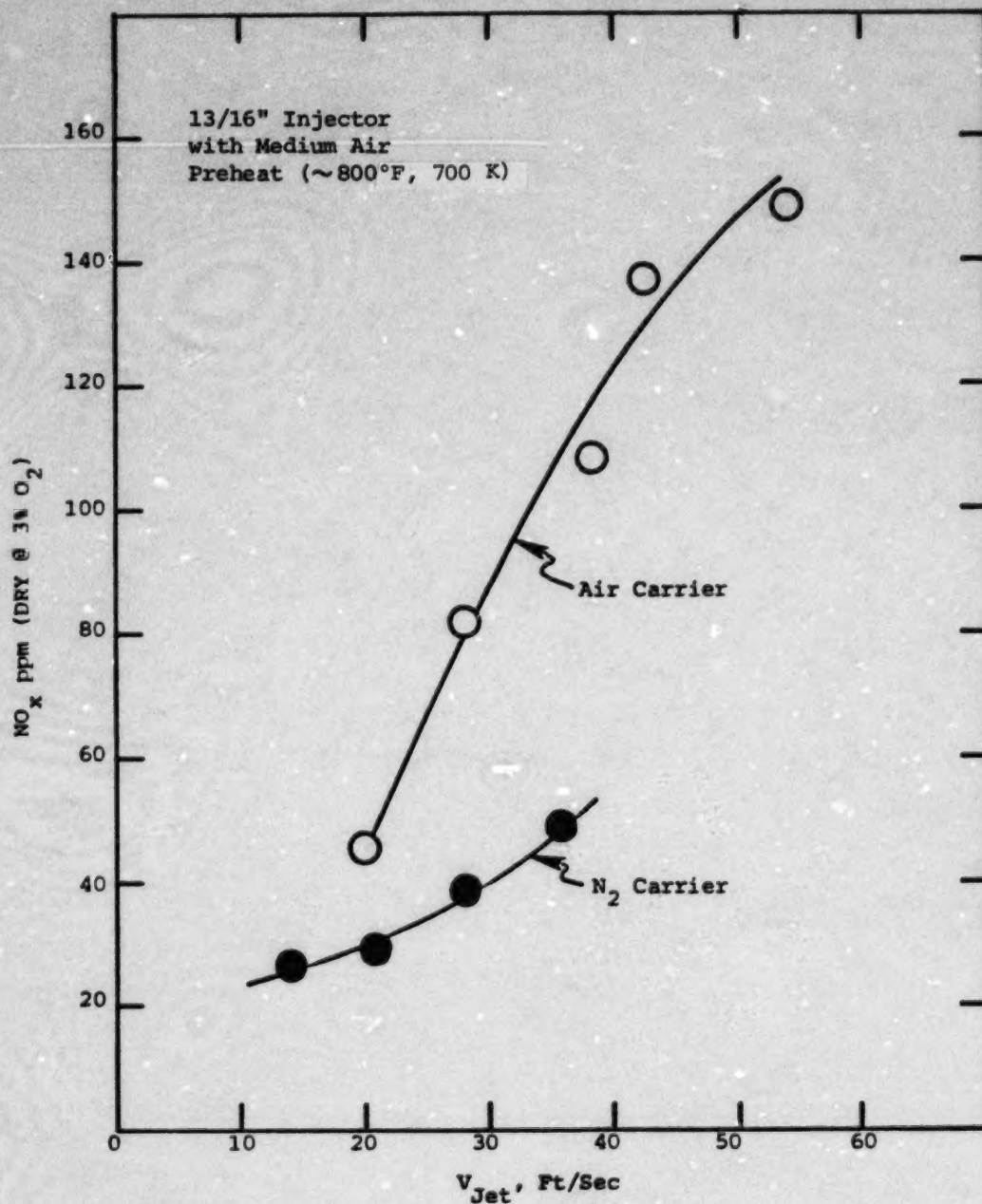


Figure 6-3. NO_x vs. Injection Velocity for Air and N_2 Carriers
Gas Fuel - 8" Furnace - HD Insulation.

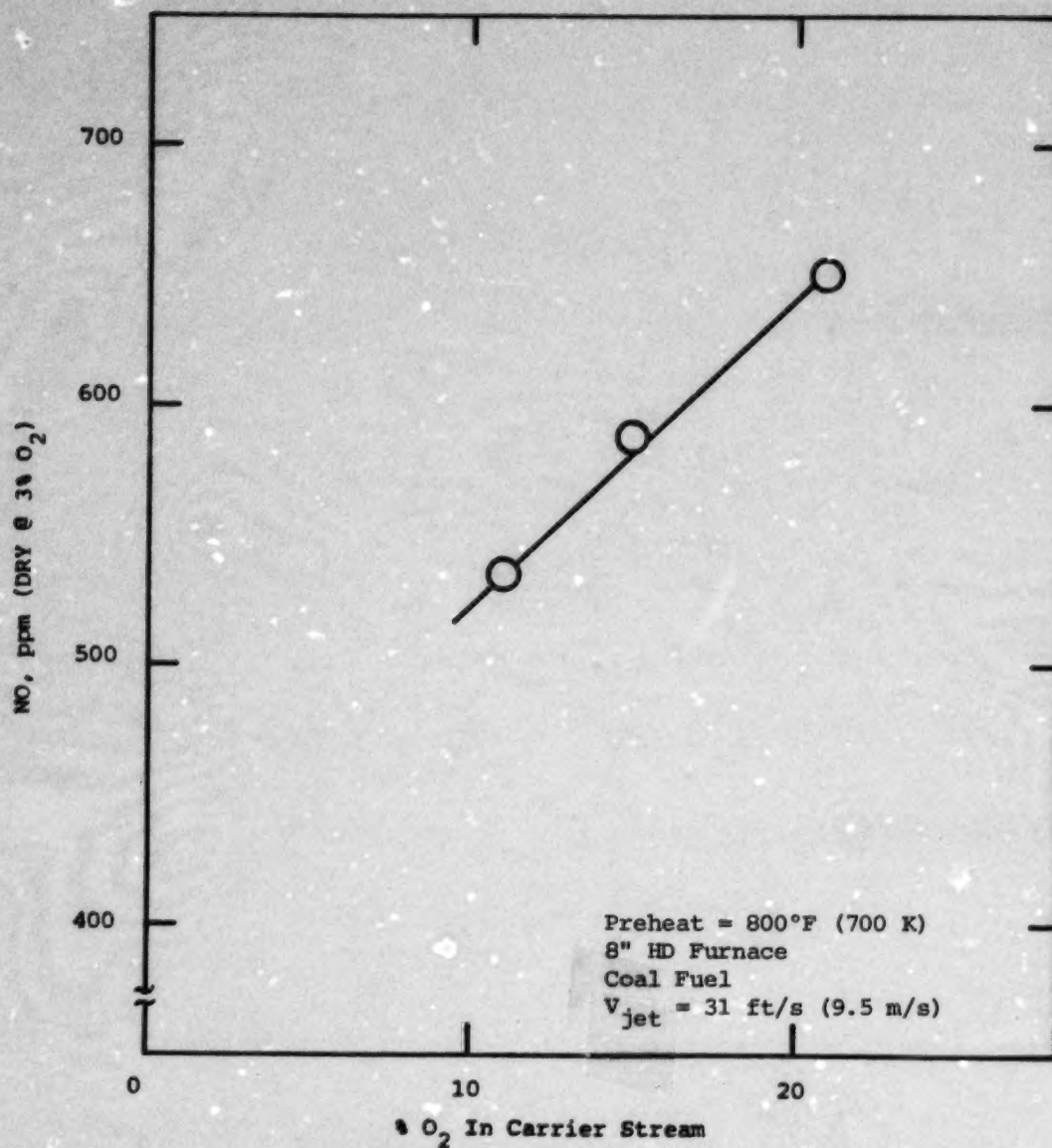


Figure 6-4. Effect of Carrier O₂ on NO_x

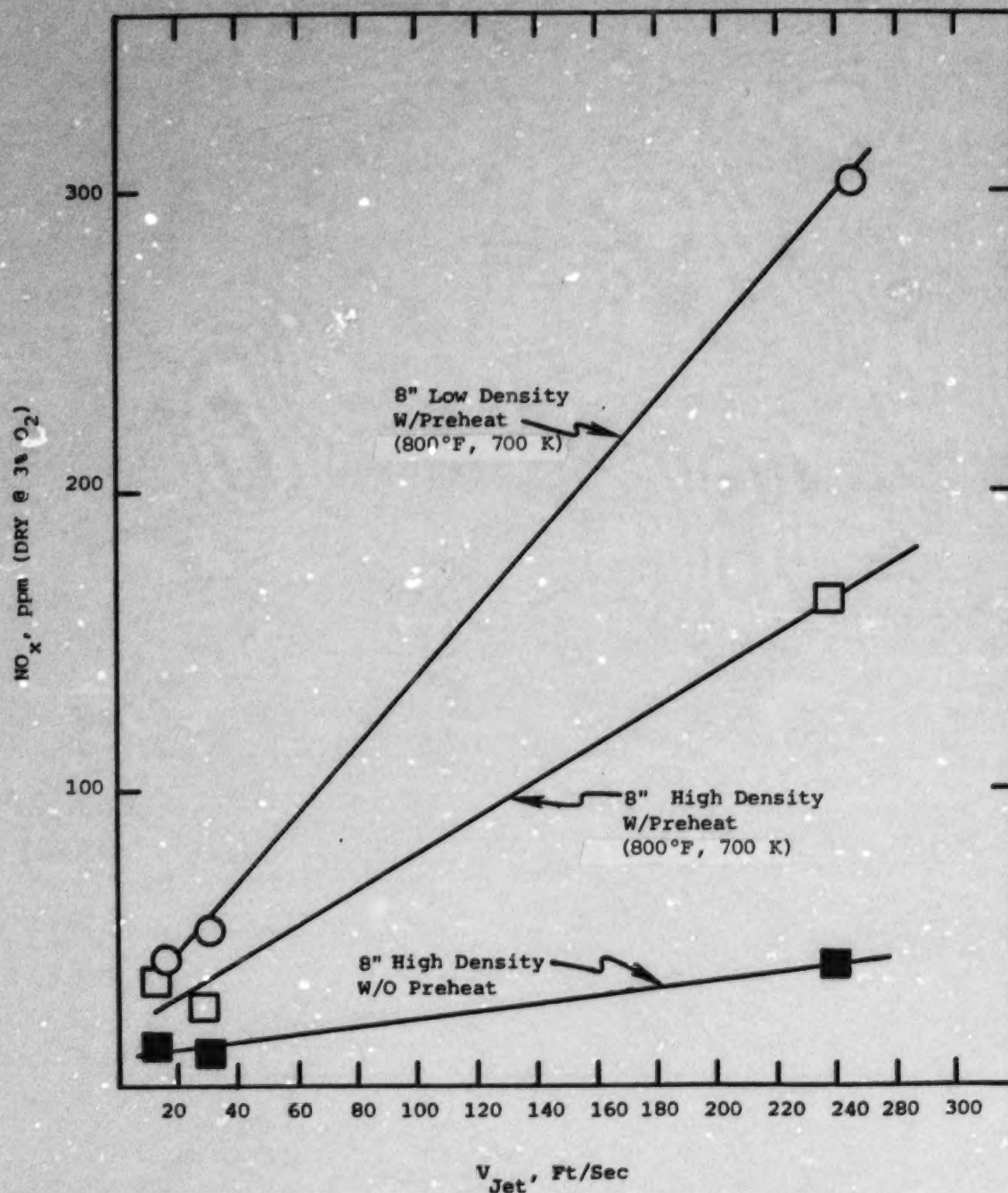


Figure 6-5. NO_x vs. Injection Velocity - Natural Gas Only.

Figure 6-6 shows the effect of preheat on NO_x emissions from coal. At the same heat input ($\sim 200,000$ Btu/hr-- 0.06 MW_t) and injection velocity (52-55 ft/sec--15.9-16.7 m/s), a moderate level of preheat increases the NO_x emissions 40 to 60 percent, depending on excess O_2 . As with the gas tests, the preheated air temperature was 800-900°F (700-756 K).

Figure 6-7 shows NO_x emissions as a function of injection velocity for gas fuel. The injection velocities were changed by varying the injector diameters. The data are presented for three levels of combustion air preheat - none, $\sim 800^\circ\text{F}$ (700 K), and $\sim 1600^\circ\text{F}$ (1144 K). The figure clearly shows the effect of high preheat upon NO_x formation. The data at high preheat suggests that the NO_x decreases at very high fuel injection velocities. This effect may be due to the decreased gas residence time within the combustor which would inhibit NO_x production. Another possible explanation would be that at very high fuel injection velocities, the mixing is so rapid that the combustion would correspond to a premixed flame for which the maximum NO_x would occur at 0 percent excess air.

The curve shown at high preheat is a quadratic regression of NO_x as a function of fuel injection velocity, i.e.:

$$\text{NO}_x = a + b v_{\text{jet}} + c v_{\text{jet}}^2$$

This function is able to account for 87 percent of the data scatter. The effect of high fuel injection velocity on NO_x is less pronounced at the lower combustion air temperatures.

Several significant variables affecting NO_x formation in cement kilns have been identified. These variables are:

- . Fuel injection velocity
- . Combustion air preheat
- . Furnace wall temperature
- . Carrier gas composition
- . Excess O_2

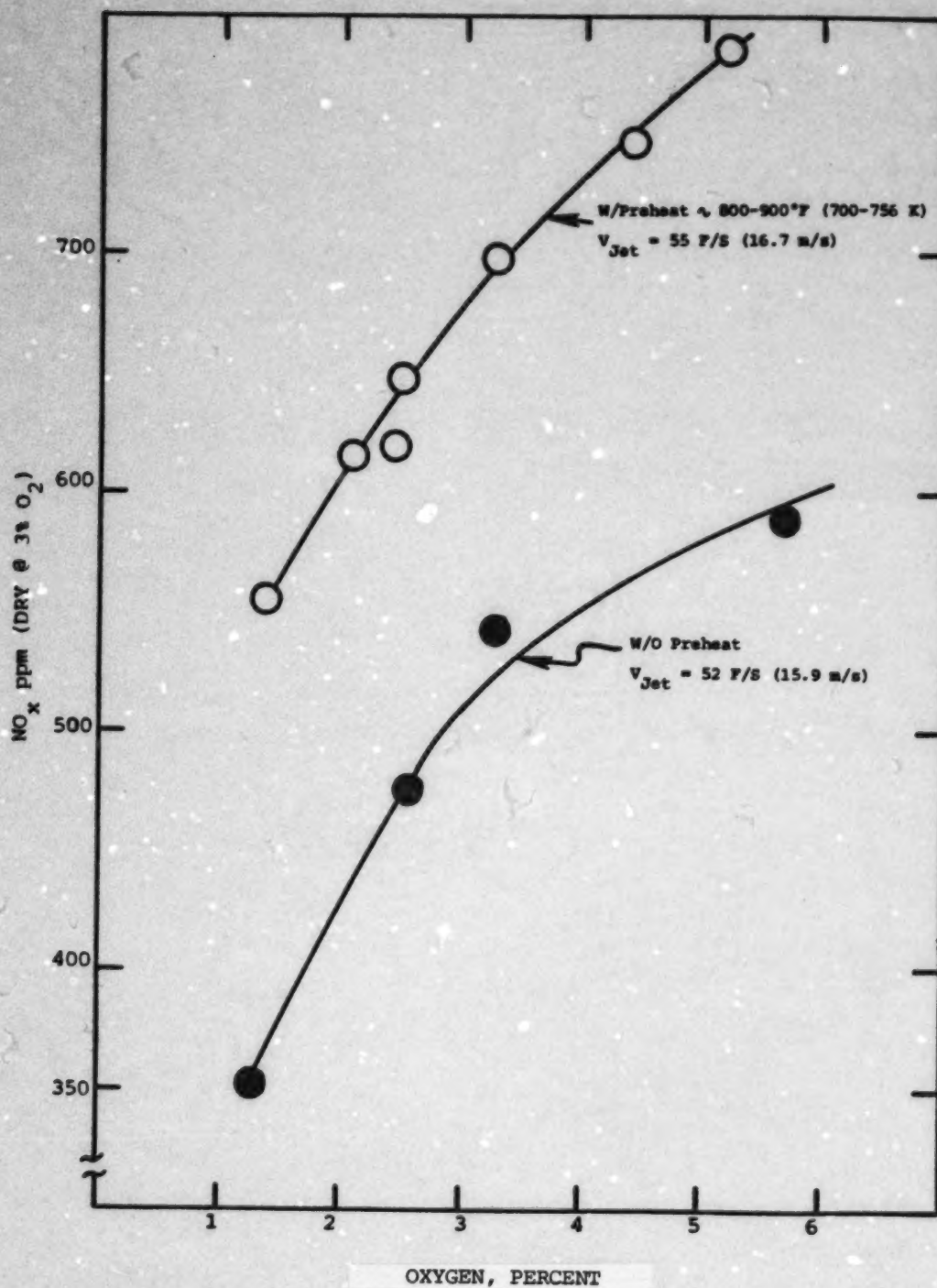


Figure 6-6. NO_x vs. O₂ - Coal-Constant V_{Jet} - 8" LD Furnace

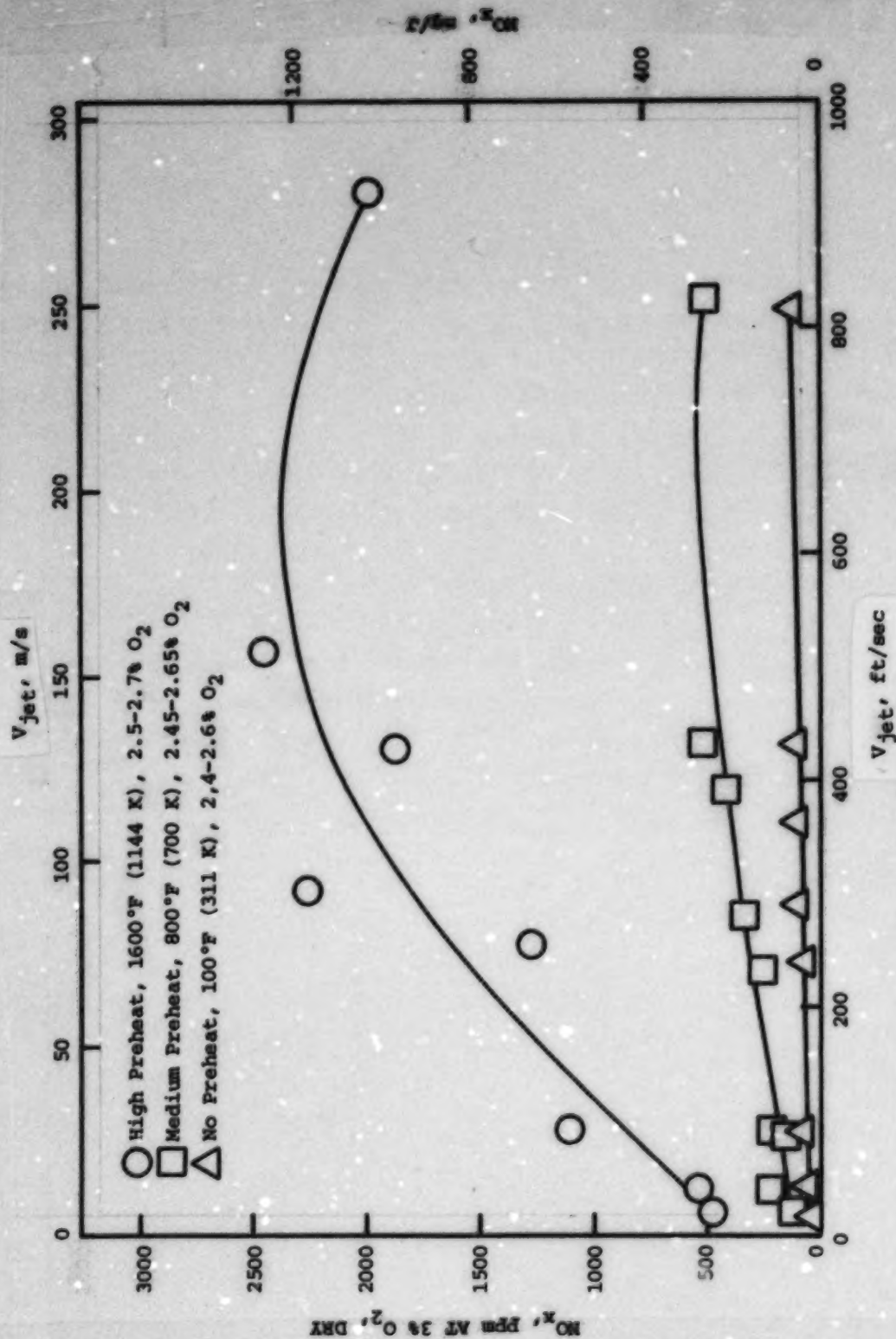


Figure 6-7. NO_x Emissions vs. Injection Velocity - Natural Gas Fuel

These results suggest a number of approaches to NO_x reduction:

- Reduce fuel injection velocity. This variable has a strong effect on NO_x emissions, but it can reduce flame geometry often essential for product quality.
- Reduce oxygen content of carrier gas. This approach would substantially lower NO_x emissions while preserving the flame geometry.
- Reduce furnace wall temperature. This can be achieved by enclosing the primary combustion zone of the flame in a water/air cooled shroud to prevent the radiation of the flame to the hot refractory or by the re-injection of cement dust in a shroud surrounding the flame to provide a heat sink for radiation from the flame and hence reduce the flame temperature.
- Distribute cold combustion air to near burner flame zone. The approach involves injecting a layer of cold air in the mixing region between the fuel/carrier jet and the preheated combustion air to act as a shield and minimize NO_x produced with high levels of preheat. Optimizing the amount of cold air would minimize the potential adverse impact on efficiency.

SECTION 7.0

REFERENCES

1. Hunter, S. C., et al., "Application of Combustion Modifications to Industrial Combustion Equipment," EPA-600/7-79-015a, January 1979.
2. Bartz, D. R., et al., "Control of Oxides of Nitrogen From Stationary Sources in the South Coast Air Basin," ARB 2-1471, September 1974.
3. State of California Air Resources Board, "Public Meeting to Consider Suggested Control Measure for the Control of Oxides of Nitrogen Emissions from Glass Melting Furnaces," September 5, 1980.
4. Anon., "Energy Conservation in the Cement Industry," Portland Cement Association, June 1975.
5. Sprung, S., Das Verhalten des Schwefels beim Brennen von Zementklinker, Beton-Verlag GmbH (1964).
6. Dickerman, J. C. and Johnson, K. L., "Technology Assessment Report for Industrial Boiler Applications: Flue Gas Desulfurization," EPA-600/7-79-1781, November 1979.

SECTION 8.0

CONVERSION FACTORS

SI Units to Metric or English Units

To Obtain	From	Multiply By	To Obtain ppm at 3% O ₂ of Natural Gas Fuel	Multiply* Concentration in ng/J by
g/Mcal	ng/J	0.004186	CO	3.23
10 ⁶ Btu	GJ	0.948	HC	5.65
Btu	gm cal	3.9685x10 ⁻³	NO or NO _x	1.96
lb/10 ⁶ Btu	ng/J	0.00233	SO ₂ or SO _x	1.41
ft	m	3.281		
in.	cm	0.3937		
ft ²	m ²	10.764		
ft ³	m ³	35.314		
lb	kg	2.205		
Fahrenheit	Celsius	$t_F = 9/5(t_C) + 32$		
Fahrenheit	Kelvin	$t_F = 1.8t_K - 460$		
psig	Pa	$P_{psig} = (P_{pa}) (1.450 \times 10^{-4}) - 14.7$		
psia	Pa	$P_{psia} = (P_{pa}) (1.450 \times 10^{-4})$		
iwg (39.2 °F)	Pa	$P_{iwg} = (P_{pa}) (4.014 \times 10^{-3})$		
10 ⁶ Btu/hr	MW	3.413		
GJ/hr	MW	3.60		
			Oil Fuel	
			CO	2.93
			HC	5.13
			NO or NO _x	1.78
			SO ₂ or SO _x	1.28
			Coal Fuel	
			CO	2.69
			HC	4.69
			NO or NO _x	1.64
			SO ₂ or SO _x	1.18

*These conversions depend on fuel composition.
The values given are for typical fuels.

English and Metric Units to SI Units

To Obtain	From	Multiply By	To Obtain ng/J of	Multiply* Concentration in ppm @ 3% O ₂ by
ng/J	lb/10 ⁶ Btu	430	Natural Gas Fuel	
ng/J	g/Mcal	239	CO	0.310
GJ	10 ⁶ Btu	1.055	HC	0.177
m	ft	0.3048	NO or NO _x (as NO ₂)	0.510
cm	in.	2.54	SO ₂ or SO _x	0.709
m ²	ft ²	0.0929		
m ³	ft ³	0.02832	Oil Fuel	
kg	lb	0.4536	CO	0.341
Celsius	Fahrenheit	$t_c = 5/9 (t_f - 32)$	HC	0.195
Kelvin	Fahrenheit	$t_k = 5/9 (t_f - 32) + 273$	NO or NO _x (as NO ₂)	0.561
Pa	psig	$P_{pa} = (P_{psig} + 14.7) (6.895 \times 10^3)$	SO ₂ or SO _x	0.780
Pa	psia	$P_{pa} = (P_{psia}) (6.895 \times 10^3)$		
Pa	iwg (39.2 °F)	$P_{pa} = (P_{iwg}) (249.1)$	Coal Fuel	
MW	10 ⁶ Btu/hr	0.293	CO	0.372
MW	GJ/hr	0.278	HC	0.213
			NO or NO _x (as NO ₂)	0.611
			SO ₂ or SO _x	0.850

*These conversions depend on fuel composition.
The values given are for typical fuels.

APPENDIX A-1.0

GASEOUS AND PARTICULATE EMISSIONS TEST METHODS AND INSTRUMENTATION

All emission measurement instrumentation was carried in a 9.8 m x 2.4 m (8 x 42 ft) mobile laboratory trailer. A plan view of the trailer is shown in Figure A-1. The gaseous species measurements were made with analyzers located in the trailer.

The emission measurement instrumentation used was the following:

TABLE A-1. EMISSION MEASUREMENT INSTRUMENTATION

Species	Manufacturer	Measurement Method	Model No.
Hydrocarbon	Beckman Instruments	Flame Ionization	402
Carbon Monoxide	Beckman Instruments	IR Spectrometer	865
Oxygen	Teledyne	Polarographic	326A
Carbon Dioxide	Beckman Instruments	IR Spectrometer	864
Nitrogen Oxides	Thermo Electron Co.	Chemiluminescent	10A
Particulates	Andersen Samplers, Inc.	EPA Method 5 Train	EPA
Sulfur Dioxide	DuPont Instruments	UV Spectrometer	400
Particle Sizing	Andersen Samplers, Inc.	Cascade Impactor	Mark III
Smoke Spot	Bacharach	ASTM 2156-65	RCC
Opacity		EPA Method 9	
Sulfur Oxides (SO _x)		Goksoyr-Ross	

A-1.1 GAS SAMPLING AND CONDITIONING SYSTEM

A flow schematic of the flue gas sampling and analyzing system is shown in Figure A-2. The sampling system uses three positive-displacement diaphragm pumps to continuously draw flue gas from the stack into the

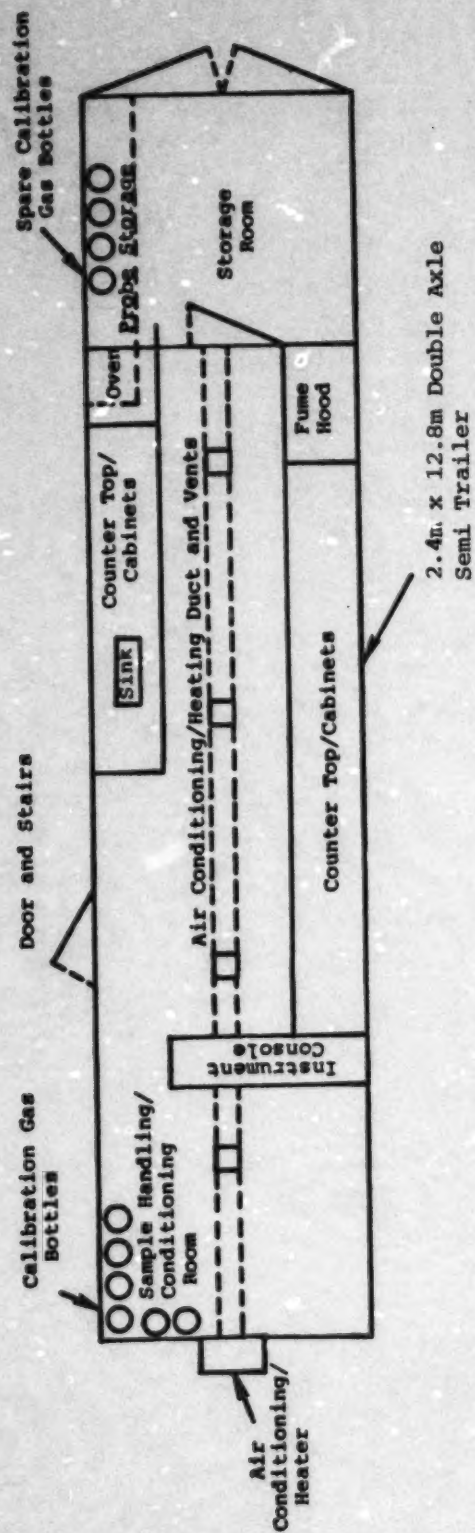


Figure A-1. Instrumentation trailer floor plan.

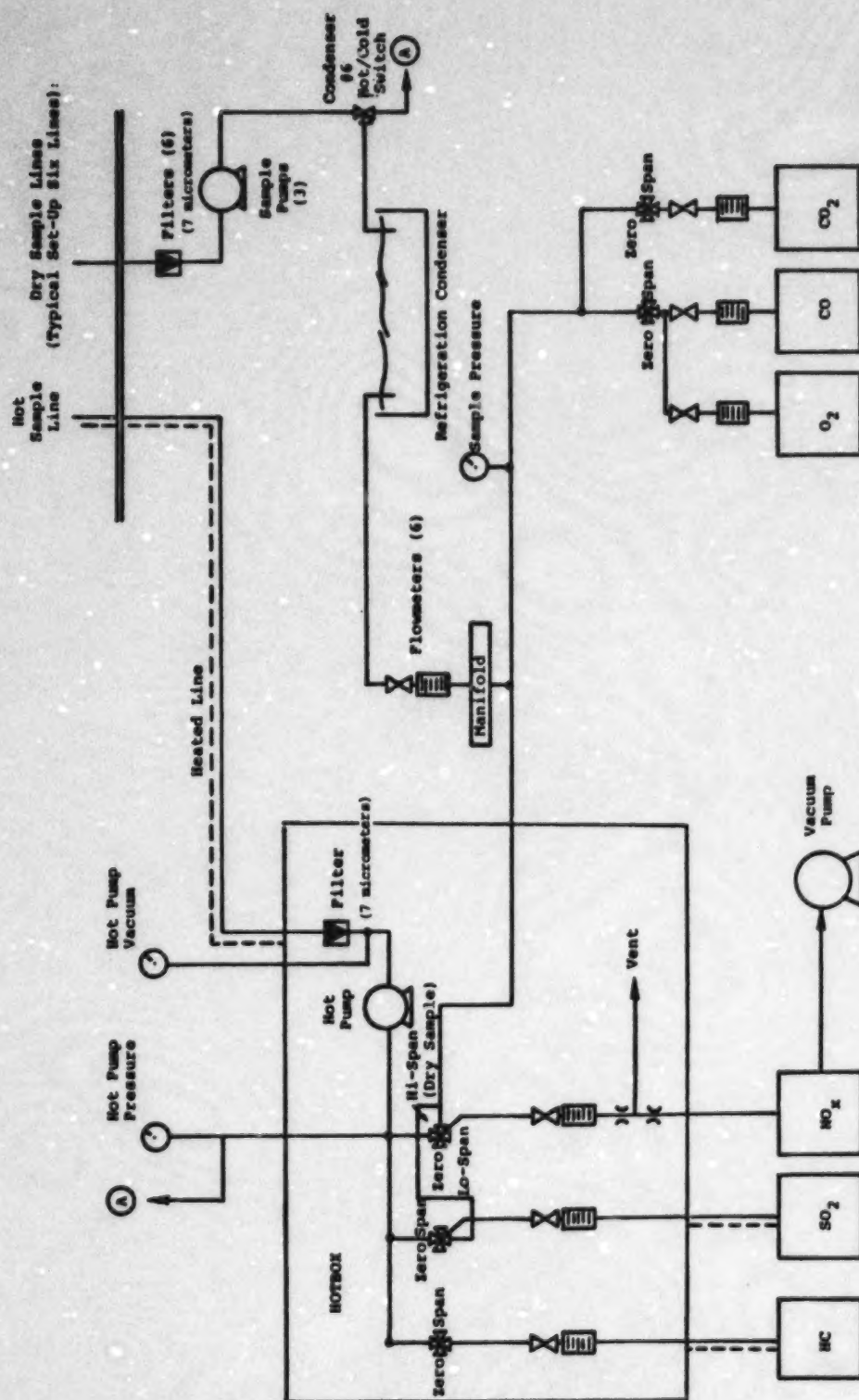


Figure A-2. Flue gas sampling and analyzing system.

laboratory. The sample pumps pull from six unheated sample lines. Selector valves allow composites of up to six points to be sampled at one time. The probes are connected to the sample pumps with 0.95 cm (3/8") or 0.64 cm (1/4") nylon line. The positive displacement diaphragm sample pumps provide unheated sample gas to the refrigerated condenser (to reduce the dew point to 35°F), a rotameter with flow control valve, and to the O₂, NO, CO, and CO₂ instrumentation. Flow to the individual analyzers is measured and controlled with rotameters and flow control valves. Excess sample is vented to the atmosphere.

To obtain a representative sample for the analysis of NO₂, SO₂ and hydrocarbons, the sample must be kept above its dew point, since heavy hydrocarbons may be condensable, and SO₂ and NO₂ are quite soluble in water. For this reason, a separate electrically-heated sample line is used to bring the sample into the mobile laboratory for analysis. The sample line is 0.95 cm (3/8-inch) Teflon line, electrically traced and thermally insulated to maintain a sample temperature of up to 478 K (400°F). A heated diaphragm pump provides hot sample gas to the hydrocarbon, SO₂ and NO_x analyzers.

A-1.2 INSTRUMENTAL CONTINUOUS MEASUREMENTS

The laboratory trailer is equipped with analytical instruments to continuously measure concentrations of NO, NO₂, CO, CO₂, O₂, SO₂, and hydrocarbons. All of the continuous monitoring instruments and sample handling system are mounted in the self-contained mobile laboratory. The entire system requires only connection to on-site water, power, and sampling lines to become fully operational. The instruments themselves are shock mounted on a metal console panel. The sample flow control measurement, and selection, together with instrument calibration are all performed from the console face. Three-pen recorders provide a continuous permanent record of the data taken. The sample gas is delivered to the analyzers at the proper condition and flow rate through the sampling and conditioning system described in the previous section. The sections below describe the analytical instrumentation.

A-1.2.1 Nitric Oxide (NO) and Total Nitrogen Oxides (NO_x)

Both the total nitrogen oxides (NO_x) and nitric oxide (NO) concentrations are measured from a sample gas obtained using a heated sample line at 394 K (250°F). In addition, the nitric oxide concentrations are measured sequentially from samples obtained using the unheated sample line that is connected to the same analyzer in the laboratory trailer. In the latter case, water is first removed from the sample gas by a refrigeration unit. The analytical instrument that is used for all of these measurements is the Thermo Electron Model 10A chemiluminescent gas analyzer.

For NO analyses, the sample gas is passed directly into the reaction chamber where a surplus of ozone is maintained. The reaction between the NO and the ozone produces light energy proportional to the NO concentration which is detected with a photomultiplier and converted to an electrical signal. Air for the ozonator is drawn from ambient through an air dryer and a 10-micrometer filter element.

The chemiluminescent reaction with ozone is specific to NO. To detect NO₂, a thermal converter has been designed to dissociate the NO₂ to NO by the bi-molecular reaction: $2 \text{NO}_2 + 2 \text{NO} + \text{O}_2$. A model 700 thermal converter is used in conjunction with the chemiluminescent gas analyzer as shown in Figure A-3. The converter is a coil of resistance-heated stainless steel tubing whose purpose is to drive the NO₂/NO ratio to its chemical equilibrium value at the converter temperature and pressure. The unit is designed to operate at a temperature of 923 K (1200 °F) and pressure of .3 kPa (10 torr). For these conditions and typical stack gas O₂ concentrations, the equilibrium NO₂ concentration is 0.2 percent of the total NO_x concentration. Therefore, when a gas sample containing any NO₂ is passed through the converter, essentially all the NO₂ would be converted to NO. The resulting total NO is then measured using the chemiluminescent analyzer and the difference between the actual NO and the "total NO" would be the sample NO₂ concentration. The "total NO" is interpreted as NO_x.

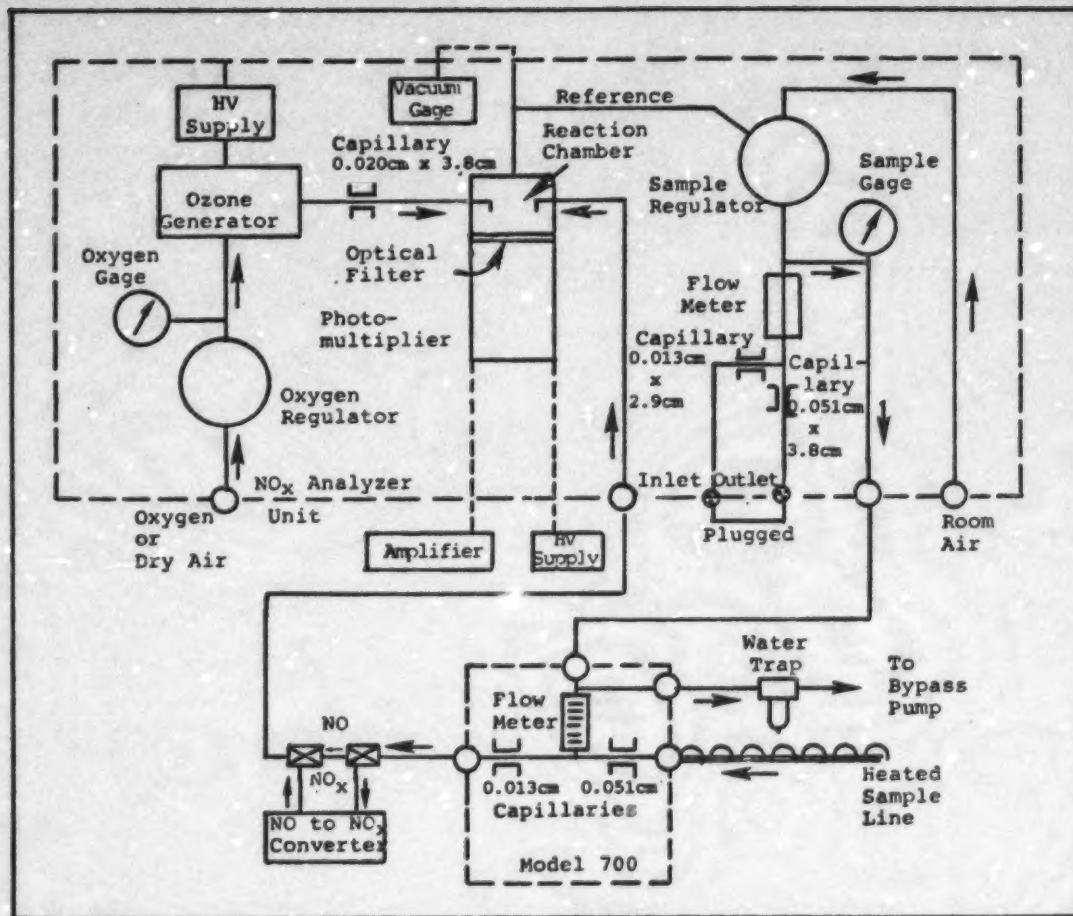


Figure A-3. Schematic of NO_x/NO chemiluminescent analysis system.

NO_2 may react upon contact with H_2O (liquid phase) to form HNO_3 (nitric acid). Under field test conditions, the exhaust gas may contain significant H_2O (depending upon the process and the ambient meteorological conditions), and it is necessary to convert the NO_2 to NO before the H_2O is allowed to condense in the sampling system. By using the heated sample line and the Thermo Electron Model 700 heated NO_x module, NO_2 concentrations will effectively be measured. In reference to Figure A-3, the sample is maintained above the H_2O dew point up to and through the 127 μm (0.005 in.) capillary in the heated module. Downstream of this capillary, the flow network is maintained at 1.3 kPa (10 torr), where the partial pressure of the H_2O in the sample is sufficiently low to prevent any condensation at ambient temperature.

When using the heated system, NO , NO_2 , and NO_x are measured on a wet basis. When not using the heated system, a condenser is placed upstream of the analyzer and NO is measured on a dry basis.

Specifications

Accuracy: 1% of full scale

Span stability: $\pm 1\%$ of full scale in 24 hours

Zero stability: ± 1 ppm in 24 hours

Power requirements: 115 $\pm$ 10V, 60 Hz, 1000 watts

Response: 90% of full scale in 1 sec (NO_x mode);

0.7 sec (NO mode)

Output: 4-20 ma

Sensitivity: 0.5 ppm

Linearity: $\pm 1\%$ of full scale

Vacuum detector operation

Range: 2.5, 10, 25, 100, 250, 1000, 2500, 10,000 ppm full scale

A-1.2.2 Carbon Monoxide and Carbon Dioxide (CO and CO₂)

Carbon monoxide and carbon dioxide concentrations are measured using Beckman Model 864 and 865 short-path-length nondispersive infrared analyzers (see Figure A-4). These instruments measure the differential in infrared energy absorbed from energy beams passed through a reference cell (containing a gas selected to have minimal absorption of infrared energy in the wavelength absorbed by the gas component of interest) and a sample cell through which the sample gas flows continuously. The differential absorption appears as a reading on a scale of 0% to 100% and is then related to the concentration of the species of interest by calibration curves supplied with the instrument. A linearizer is supplied with each analyzer to provide a linear output over the range of interest. The operating ranges for the CO analyzer are 0-100 and 0-2000 ppm, while the ranges for the CO₂ analyzer are 0-5% and 0-20%.

Specifications

Span stability: $\pm 1\%$ of full scale in 24 hours

Zero stability: ± 1 ppm in 24 hours

Ambient temperature range: 273 to 322 K (32°F to 120°F)

Line voltage: 115 $\pm$ 15V rms

Response: 90% of full scale in 0.5 or 2.5 sec

Linearity: Linearizer board installed for one range

Precision: $\pm 1\%$ of full scale

Output: 4-20 ma

A-1.2.3 Oxygen (O₂)

A Teledyne Model 326A oxygen analyzer is used to automatically and continuously measure the oxygen content of the flue gas sample. The analyzer utilizes a micro-fuel cell which is specific for oxygen, has an absolute zero, and produces a linear output from zero through 25 percent oxygen. The micro-fuel cell is a sealed electrochemical transducer with no electrolyte to change or electrodes to clean. Oxygen in the flue gas diffuses through a Teflon membrane and is reduced on the surface of the cathode. A corresponding

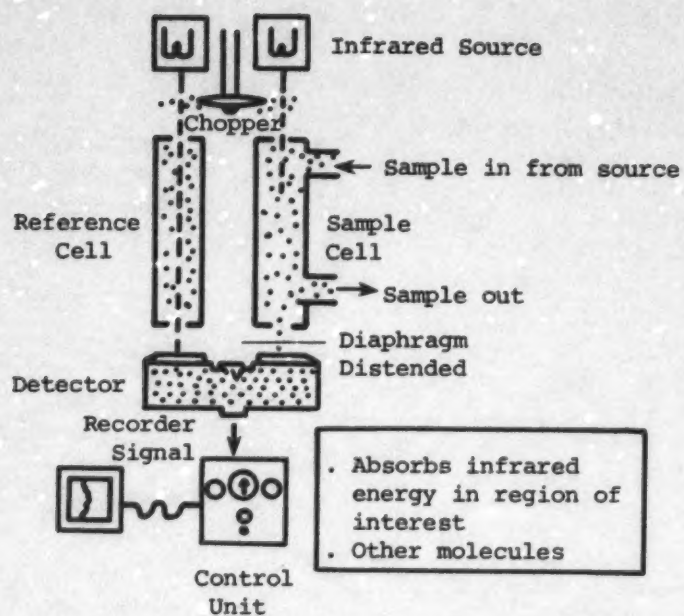


Figure A-4. Schematic of NDIR analyzer.

oxidation occurs at the anode internally and an electric current is produced that is proportional to the concentration of oxygen. This current is measured and conditioned by the instrument's electronic circuitry to give an output in percent O₂ by volume for operating ranges of 0% to 5%, 0% to 10%, and 0% to 25%.

Specifications

Precision: $\pm 1\%$ of full scale

Response: 90% in less than 40 sec

Sensitivity: 1% of low range

Linearity: $\pm 1\%$ of full scale

Ambient temperature range: 273 K to 325 K (32°F to 125°F)

Fuel cell life expectancy: 40,000+ hrs

Power requirement: 115 VAC, 50-60 Hz, 100 watts

Output: 4-20 ma

A-1.2.4 Total Hydrocarbons (HC)

Hydrocarbon emissions are measured using a Beckman Model 402 high-temperature hydrocarbon analyzer. The analyzer utilizes the flame ionization method of detection which is a proven technique for a wide range of concentrations (0.1 to 120,000 ppm). A flow schematic of the analyzer is presented in Figure A-5. The sensor is a burner where a regulated flow of sample gas passes through a flame sustained by regulated flows of air and a premixed hydrogen/nitrogen fuel gas. Within the flame the hydrocarbon components of the sample stream undergo a complex ionization that produces electrons and positive ions. Polarized electrodes collect these ions, causing current to flow through electronic measuring circuitry. Current flow is proportional to the rate at which carbon atoms enter the burner.

The analysis occurs in a temperature-controlled oven. The sample is extracted from the stack with a stainless steel probe which has been thermally treated and purged to eliminate any hydrocarbons existing in the probe itself. An insulated heat-traced teflon line is used to transfer the sample

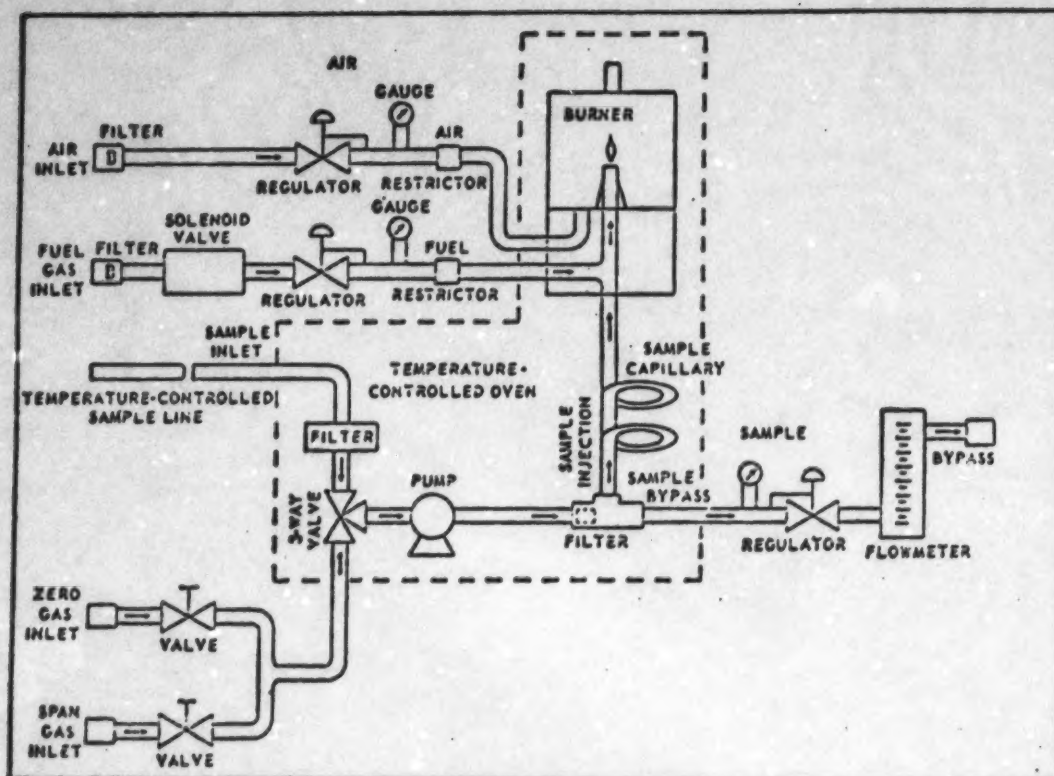


Figure A-5. Flow schematic of hydrocarbon analyzer (FID).

to the analyzer. The entire heated network is maintained at a temperature sufficient to prevent condensation of heavier hydrocarbons.

The flame ionization detector is calibrated with methane, and the total hydrocarbon concentration is reported as the methane equivalent. FID's do not respond equally to all hydrocarbons but generally provide a measure of the carbon-hydrogen bonds present in the molecule. The FID does not detect pure carbon or hydrogen.

Specifications

Full-scale sensitivity: adjustable from 5 ppm CH₄ to 10% CH₄

Ranges: Range multiplier switch has 8 positions: X1, X5, X10, X50, X100, X500, X1000, and X5000. In addition, span control provides continuously variable adjustment within a dynamic range of 10:1

Response time: 90% full scale in 0.5 sec

Precision: $\pm 1\%$ of full scale

Electronic stability: $\pm 1\%$ of full scale per 24 hours with ambient temperature change of less than 5.6 K (10°F)

Reproducibility: $\pm 1\%$ of full scale for successive identical samples

Analysis temperature: ambient

Ambient temperature: 273 K to 317 K (32°F to 100°F)

Output: 4-20 ma

Air requirements: 250 to 400 cc/min of clean, hydrocarbon-free air, supplied at 2.07×10^5 to 1.38×10^6 n/m² (30 to 200 psig)

Fuel gas requirements: 75 to 80 cc/min of fuel consisting of 100 percent hydrogen supplied at 2.07×10^5 to 1.38×10^6 n/m² (30 to 200 psig)

Electric power requirements: 120 V, 60 Hz

Automatic flame indication and fuel shut-off valve

A-1.2.5 Sulfur Dioxide (SO₂)

A Dupont Model 400 photometric analyzer is used for measuring SO₂. This analyzer measures the difference in absorption of two distinct wavelengths (ultraviolet) by the sample. The radiation from a selected light source passes through the sample and then into the photometer unit where the radiation is split by a semi-transparent mirror into two beams. One beam is directed to a phototube through a filter which removes all wavelengths except the "measuring" wavelength, which is strongly absorbed by the constituent in the sample. A second beam falls on a reference phototube, after passing through an optical filter which transmits only the "reference" wavelength. The latter is absorbed only weakly, or not at all, by the constituent in the sample cell. The phototubes translate these intensities to proportional electric currents in the amplifier. In the amplifier, full correction is made for the logarithmic relationships between the ratio of the intensities and concentration or thickness (in accordance with Beer's Law). The output is therefore linearly proportional, at all times, to the concentration and thickness of the sample. The instrument has a lower detection limit of 2 ppm and full scale ranges of 0-200 and 0-2000 ppm.

Specifications

Noise: Less than 1/4%

Drift: Less than 1% full scale in 24 hours

Accuracy: ($\pm 1\%$ of analyzer reading) + ($\pm 1/4\%$ of full scale range)

Sample cell: 304 stainless steel, quartz windows

Flow rate: 0.05 dm³/s (6 cfh)

Light source: Either mercury vapor, tungsten, or "Osram"
discharge type lamps

Power rating: 500 watts maximum, 115 V, 60 Hz

Reproducibility: 1/4% of scale
Electronic response: 90% in 1 sec
Sample temperature: 378 K (220°F)
Output: 4-20 ma d.c.

A-1.3 PARTICULATE MATTER TOTAL MASS CONCENTRATION

Particulate matter is collected by filtration and wet impingement in accordance with US-EPA Method No. 5. Nomograph techniques are utilized to select the proper nozzle size and to set the isokinetic flow rates.

Gas samples for particulate sampling can be taken from the same sample port as those for gas analysis and passed through the Joy Manufacturing Company Portable Effluent Sampler. This system, which meets the EPA design specifications for Test Method 5, Determination of Particulate Emissions from Stationary Sources (Federal Register, Volume 36, No. 27, page 24888, December 24, 1971, and revisions thereof) is used to perform both the initial velocity traverse and the particulate sample collection.

Dry particulates are collected in the heated case that may contain a cyclone to separate particles larger than 5 μm and a 110-mm glass-fiber filter to retain particles as small as 0.3 μm . Condensible particulates are collected in four Greenburg-Smith impingers immersed in a chilled water bath.

The sampling probe is positioned through an exhaust port and attached to the sampling box. The probe consists of a sampling nozzle, heated probe, gaseous probe, thermocouple, and pitot tube. The ball joint from the heated probe connects to the cyclone and glass filter holder assembly. These assemblies are positioned in the heated sampling box which is maintained at 394 K (250°F), in order to eliminate condensation. The sample then passes from the heated section to four Greenburg-Smith impingers immersed in an ice bath. Only the second impinger has the original tip, the other three have had the tip removed to decrease the pressure drop through them. The first and second impingers are filled with 150 milliliters of distilled/deionized water. The third impinger is left dry. The fourth impinger is filled with approximately 200 grams of indicating silica gel to remove entrained water. The use of

silica gel assures that a dry sample is delivered to the meter box. After sampling, the spent silica gel is discarded and not used for any further analysis.

An umbilical cord connects the last impinger, the pitot tube, and the heating elements to the meter box which is located in a convenient place within 15 m of the sampling ports. The meter box contains a vacuum pump, regulating valves, instantaneous and integrating flow meters, pitot tube manometers, vacuum gauge, and electrical controls.

Particulate matter (solids and condensibles) is collected in three discrete portions by the sampling train: the probe and glassware upstream of the filter; the filter; and the wet impingers. The probe and glassware are brushed and rinsed with acetone; the matter is captured for gravimetric analysis. The probe and glassware are then rinsed with distilled water and the rinsings transferred to a second container for analysis. The filter is desiccated and analyzed gravimetrically. The combined impinger liquid is heated to drive off uncombined water and the residue retained for analysis. The particulate matter analysis is illustrated schematically in Figure A-6.

US EPA Method 5 considers the particulate matter captured in containers (1) and (3); the filter, probe brushing, and probe acetone rinse. As EPA source standards are based on solid particulates only, care is taken to differentiate between solid and the total (including condensible) particulates. The water wash is performed because KVB's test experience has shown that a significant amount of water-soluble material may sometimes be captured by the probe.

The dry sample volume is determined with a dry test meter at a measured temperature and pressure and then converted to standard conditions. The volume of condensed water in the impingers is measured in milliliters and the corresponding volume of water vapor is then computed at standard conditions. The dry sample volume and water vapor volume are then summed to give the total sample volume. The dry sample volume is used in the data reduction procedures.

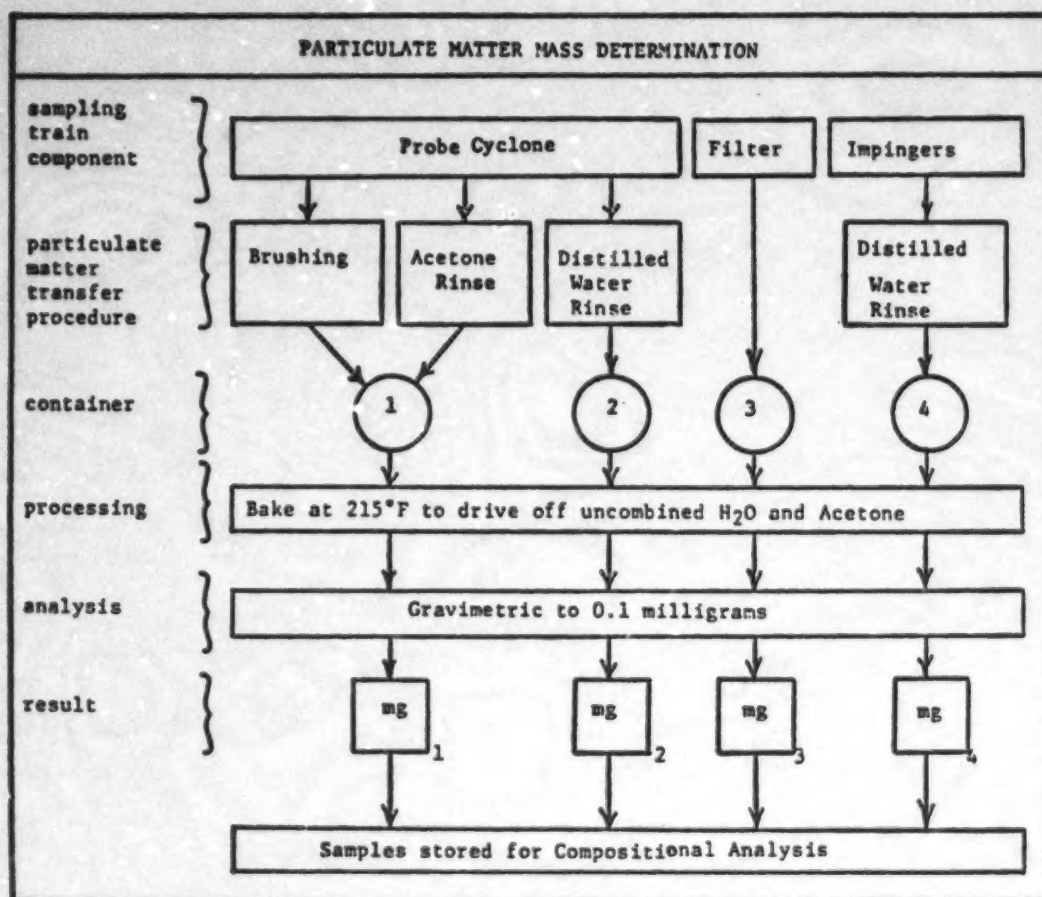


Figure A-6. Processing and analyzing particulate matter.

A point of interest is the method chosen to calculate particulate emissions in ng/J or lb/10⁶ Btu from the experimental data. The particulate sampling train, properly operated, yields particulate mass per unit flue gas volume. Having measured g/m³, it is necessary to establish the flue gas volume per unit heat input if emissions in ng/J are desired. The original Method 5 involved determining a velocity traverse of the stack, the cross-sectional area, the flue flow rate, and fuel heating value. A revised and more accurate method has been promulgated by the Environmental Protection Agency that utilizes a fuel analysis (carbon content, hydrogen content, high heating value, etc.) and the measured O₂ in the exhaust to calculate the gas volume generated in liberating 1.055 GJ (one million Btu's). The velocity traverse approach generally results in a 20 to 30 percent higher value and is believed to be less accurate.

A-1.4 SMOKE SPOT

On combustion equipment where smoke numbers normally are taken, such as oil-fired boilers, KVB, Inc. determines the smoke number using test procedures according to ASTM Designation: D 2156-65. The smoke number is determined at each combustion modification setting of the unit. Examples are baseline, minimum excess air, low load, etc., and whenever a particulate concentration is measured.

Smoke spots are obtained by pulling a fixed volume of flue gas through a fixed area of a standard filter paper. The color (or shade) of the spots that are produced is visually matched with a standard scale. The result is a "Smoke Number" which is used to characterize the density of smoke in the flue gas.

The sampling device is a hand pump similar to the one shown in Figure A-7. It is a commercially available item that can pass $36,900 \pm 1650$ cu cm of gas at 289K and 1 atmosphere pressure through an enclosed filter paper for each 6.5 sq cm effective surface area of the filter paper.

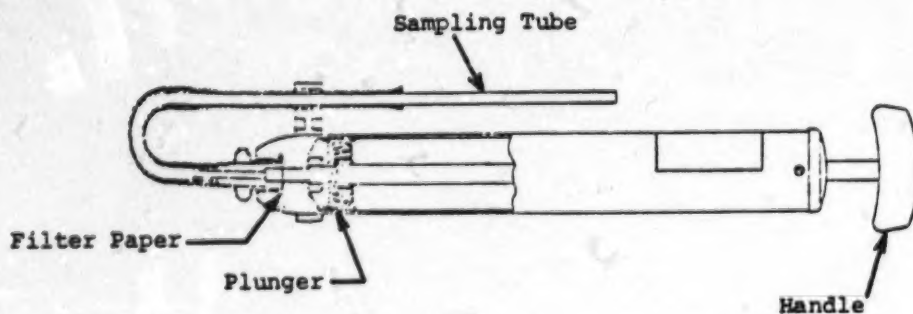


Figure A-7. Field-service-type smoke tester.

The smoke spot sampler is provided with a motor-driven actuator to ensure a constant sampling rate independent of variations in stroke rate that can occur when the sampler is operated manually.

The smoke scale required consists of a series of ten spots numbered consecutively from 0 to 9, and ranging in equal photometric steps from white through neutral shades of gray to black. The spots are imprinted or otherwise processed on white paper or plastic stock having an absolute surface

reflectance of between 82.5 and 87.5%, determined photometrically. The smoke scale spot number is defined as the reduction (due to smoke) in the amount of light reflected by a soiled spot on the filter divided by 10.

Thus the first spot, which is the color of the unimprinted scale, is No. 0. In this case there is no reduction in reflected incident light directed on the spot. The last spot, however, is very dark, reflecting only 10% of the incident light directed thereon. The reduction in reflected incident light is 90%, and this spot is identified as No. 9. Intermediate spot numbers are similarly established. Limits of permissible reflectance variation of any smoke scale spot will not exceed $\pm 3\%$ relative reflectance.

The test filter paper is made from white filter paper stock having absolute surface reflectance of 82.5 to 87.5%, as determined by photometric measurement. When making this reflectance measurement, the filter paper is backed by a white surface having absolute surface reflectance of not less than 75%.

When clean air at standard conditions is drawn through clean filter paper at a flow rate of 47.6 cu cm per sec per sq cm effective surface area of the filter paper, the pressure drop across the filter paper falls between the limits of 1.7 and 8.5 kPa (1.3 and 6.4 cm of mercury).

The sampling procedure is exactly that specified in D 2156. A clean, dry, sampling pump is used. It is warmed to room temperature to prevent condensation on the filter paper. When taking smoke measurements in the flue pipe, the intake end of the sampling probe is placed at the center line of the flue. When drawing the sample, the pressure in the flue gas stream and the sampler is allowed to equalize after each stroke.

The smoke density is reported on the Mobile Lab Data Sheet as the Smoke Spot Number on the standard scale most closely corresponding to test spot. Differences between two standard Smoke Spot Numbers are interpolated to the nearest half number. Smoke Spot Numbers higher than 9 are reported as "Greater than No. 9."

This procedure is deemed to be reproducible to within $\pm 1/2$ of a Smoke Spot Number under normal conditions where no oily stain is deposited on the disk.

KVB's field experience with industrial boilers has been that the human factor involved in the interpretation of the smoke spot by an experienced observer does not cause a significant lack of precision.

A-1.5 OPACITY

Opacity readings are taken by a field crew member who is a certificated graduate of a U.S. Environmental Protection Agency approved "Smoke School". Observations are made at the same time that particulate measurements are made and as often in addition as deemed necessary to gather the maximum amount of information. The procedures set forth in EPA Method 9, "Visual Determinations of the Opacity of Emissions for Stationary Sources" are followed.

Observations are made and recorded at 15 second intervals while particulate concentration is being measured and after the unit has stabilized at other times. Before beginning observations, the observer determines that the feedstock or fuel is the same as that from which the sample was taken for the fuel analysis.

Before beginning opacity observations, the observer makes arrangements with the combustion unit operator to obtain the necessary process data for the standard KVB Control Room Data Sheet. The control room data are recorded for the entire period of observations, as is customarily done by KVB during an emissions test. The process unit data that are obtained include:

- a. Production rates
 - 1. maximum rated capacity
 - 2. actual operating rate during test
- b. Control device data
 - 1. recent maintenance history
 - 2. cleaning mechanism and cycle information

The observer requests the appropriate plant personnel to briefly review and comment on the opacity measurements and process data and the observer comments on:

- a. the basis for choosing the observation periods used.
- b. why it is believed the periods chosen constitute periods of greatest opacity.
- c. why the observations span a time period sufficient to characterize the opacity.

Consideration is given to postponing the EPA Method 5 particulate tests during periods of cloudy or rainy weather because of the inability of the observer to monitor the smoke.

A-1.5.1 Sulfur Oxides (SO_x)

Goksoyr-Ross Method--Wet Chemical Method

The Goksoyr-Ross Controlled Condensate (G/R) method is used for the wet chemical SO_2/SO_3 determination. It is a desirable method because of its simplicity and clean separation of particulate matter, SO_2 and H_2SO_4 (SO_3). This procedure is based on the separation of H_2SO_4 (SO_3) from SO_2 by cooling the gas stream below the dew point of H_2SO_4 but above the H_2O dew point. Figure A-8 illustrates schematically the G/R test system.

Particulate matter is first removed from exhaust gas stream by means of a quartz glass filter placed in the heated glass filter holder. Tissue-quartz filters are recommended because of their proven inertness to H_2SO_4 . The filter system is heated by a heating tape so that the gas out temperature of 533 K (500°F) is maintained. This temperature is imperative to ensure that none of the H_2SO_4 will condense in the filter holder or on the filter.

The condensation coil where the H_2SO_4 is collected is cooled by water which is maintained at 333 K (140°F) by a heater/recirculator. This temperature is adequate to reduce the exhaust gas to below the dew point of H_2SO_4 .

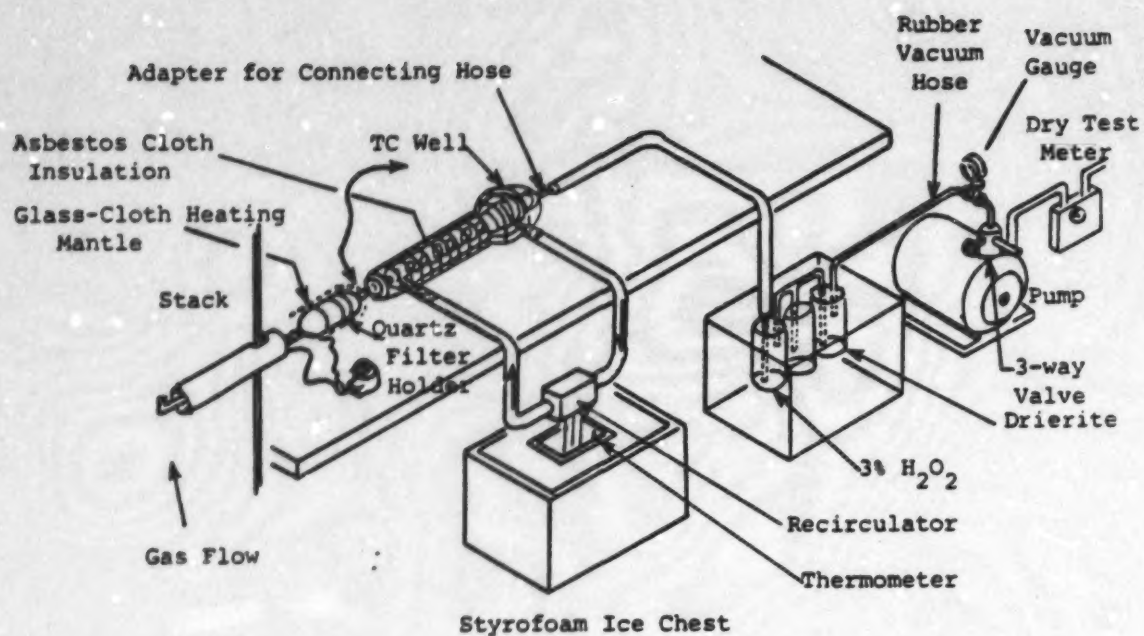


Figure A-8. Schematic of Goksoyr-Ross controlled condensation system (CCS).

Three impingers are shown in Figure A-8. The first impinger is filled with 3 percent H_2O_2 to absorb SO_2 . The second impinger is to remove carryover moisture and the third contains Drierite and a thermometer to measure the exhaust gas temperature to the dry gas meter and pump. The sampling rate is $0.04 \text{ dm}^3/\text{s}$ (0.08 cfm).

A-1.5.2 Analysis Procedure

For both SO_2 and H_2SO_4 determination, the analytical procedure is identical. The H_2SO_4 sample is washed from the back part of the filter holder and the coil using a 5 percent isopropyl alcohol solution. The sample from the first impinger which is assumed to be absorbed and reacted SO_2 in the form of H_2SO_4 is recovered with distilled water washing. The amount of H_2SO_4 in the condensate from the coil and from the H_2O_2 impinger is measured by H^+ titration. Bromphenol Blue is used with NaOH as the titrant.

A-1.6 PARTICLE SIZE DISTRIBUTION

An Anderson Mark III in stack particle fractionating sampler was used for the particle size distribution tests (Figure A-9).

A-1.6.1 Design

The Anderson stack sampling has been designed to operate with the EPA Method 5 train. The stack head consists of a stainless steel case and 1/2" (1.3 cm) NPT female pipe fittings. The stack sampler contains nine jet plates, each having a pattern of precision drilled orifices. Special collection substrates, (e.g., glass fiber, aluminum foil, etc.) placed on the jet/collection plates, permit lighter tare weights for gravimetric analyses and a variety of collection materials for chemical analysis. The sampler may be used with or without the collection substrate. The nine plates are separated by 2.5 millimeter stainless steel spacers. The jets on each plate are arranged in modified concentric circles which are offset on each succeeding plate. The size of the orifices is the same on a given plate, but smaller for each succeeding downstream plate. Therefore, as the sample is drawn through the sampler at a constant flow rate, the jets of air flowing through any

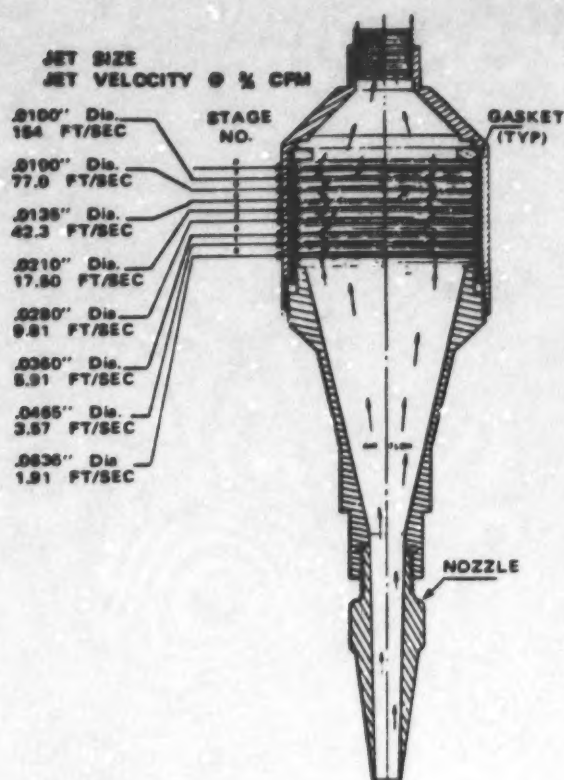


Figure A-9.
Impactor Head

particular plate direct the particles toward the collection substrate on the downstream plate directly below the circles of jets on the plate above. Since the jet diameters decrease from plate to plate, the velocities increase such that whenever the velocity imparted to a particle is sufficiently great, its inertia will overcome the aerodynamic drop of the turning air stream and the particle will be impacted on the collection substrate. Otherwise, the particle remains in the air stream and proceeds to the next plate.

Since the particle deposit areas are directly below the jets, seven of the plates act as both a jet stage and a collection plate. Thus, No. 0 plate is only a jet stage and No. 8 plate is only a collection plate.

The stack sampler is designed to operate at $0.35 \text{ dm}^3/\text{s}$ (0.75 acfm) or less. An optimum flow rate is around $0.24 \text{ dm}^3/\text{s}$ (0.5 acfm).

A-1.6.2 Operation

An EPA Method 5 train is used to draw a sample of the flue gas through the impactor. All particles entrained in the air stream are inertially impacted on the preweighed collection surfaces. The size ranges of particles deposited is from >10 microns with preseparator to <0.4 microns on the last stage. It is recommended that the preseparator be used to remove the larger particles when conditions warrant and it is necessary to use a backup filter always to ensure total collection. The collection media used during the test series were glass fiber filters. The filters were preconditioned for weighing before and after a sampling cycle in a desiccator.

Normal sampling periods vary from a few minutes to several hours depending on the grain loading situation. Ten milligrams of particulate matter on any one plate represents an approximate upper limit because of re-entrainment problems. Overloading the sampler can be detected easily by visual inspection and occurs more often during the first test at an unfamiliar stack. After the sampling cycle has been completed, the sampler is disassembled. After the desiccating of the collection media, weighing is performed to determine the net particulate accumulations.

A-1.6.3 Data Presentation

To determine the concentration of particulates for any size range, first determine the percentage of total particulates for each stage. Then the cumulative percentage is determined beginning with the last stage of the impactor. By plotting the effective cutoff diameter (ECD) and the cumulative percent on logarithmic probability graph paper, then the particle concentration by weight for any specific size can be determined.